Supporting Information belonging to the Manuscript entitled:

Visible Light Enhanced Selective Reductive Elimination of Methylmanganese Complex from Heterodinuclear Dimethylphenyl(4,4´-di-*tert*-butyl-2,2´-bipyridine)platinum-pentacarbonylmanganese Complex

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Experimental Details

General. All manipulations were carried out under dry nitrogen or argon atmosphere using standard Schlenk and vacuum line techniques. Solvents were refluxed over and distilled from appropriate drying agents under N_2: benzene, toluene, hexane, and THF from sodium benzophenone ketyl. Deuterated solvents were degassed by three freeze-pump-thaw cycles and then vacuum transferred from appropriate drying agents (C_6D_6, toluene-d_8 and THF-d_8 from sodium wire, acetone-d_6 from drierite, CD_2Cl_2 from P_2O_5). 2,2′-Bipyridine and 4,4′-di-*tert*-butyl-2,2′-bipyridine were purchased from commercial suppliers and used as received. $PtIMe_2R(bpy)$ (R = Me,[1] Et,[2] Ph[3]) and $PtMe_3(NO_3)(bpy)$[1] were prepared according to the analogous literature methods. NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^1H, 121.6 MHz for ^{31}P) and ECX-400 spectrometer (399.8 MHz for ^1H, 161.8 MHz for ^{31}P, 100.5 MHz for ^{13}C). Chemical shifts were reported in ppm downfield from TMS for ^1H and ^{13}C and from 85% H_3PO_4 in D_2O for ^{31}P. IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr disks. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer. Molar electric conductivity was measured on a TOA Conduct Meter CM 7B. UV-vis spectra were recorded on a SHIMADZU MultiSpec-1500. The irradiation system constructed with Optical Module X (model SX-UI500 MQQ) and a power supply unit (model BA-H500) was obtained from USIO Electronics All of the calculations were performed using the molecular orbital program package Spartan 6.0.

Preparation of triorgano(chrolo)(4,4´-di-*tert*-butyl-2,2´-bipyridine)platinum

$PtIMe_3(^tBu_2bpy)$. This complex was prepared by the reaction of $[PtIMe_3]_4$ and $^tBu_2bpy$ according to the analogous literature methods with modifications.[1] Yield: 90% (350.2 mg, 0.5511 mmol). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 0.61 (s, $^2J_{PtH}$ = 73.6 Hz, 3H, Pt-CH_3 trans to I), 1.44 (s, 18H, ^{t}Bu), 1.51 (s, $^2J_{PtH}$ = 70.0 Hz, 6H, Pt-CH_3 trans to N), 7.58 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, $^tBu_2bpy$-H^5), 8.11 (d, $^4J_{HH}$ = 2 Hz, 2H, $^tBu_2bpy$-H^3), 8.87 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, $^tBu_2bpy$-H^6).

$PtIMe_2R(^tBu_2bpy)$ (R = Et, ^{i}Pr, Np, ^{n}Hex, Ph, C_6H_4OMe-*p*). These complexes were prepared according to the analogous literature methods with modifications.[2]

$PtIMe_2Et(^tBu_2bpy)$. This complex was prepared analogously to by the reaction of $PtMe_2(^tBu_2bpy)$ (87.3 mg, 0.177 mmol) with EtI (200 μl, 2.49 mmol). Yield: 98% (112.9 mg, 0.174 mmol). ^1H NMR (acetone-d_6, 400 MHz, rt): δ 0.03 (t, $^3J_{PtH}$ = 66.9 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-$CH_2C$$H_3$), 1.33 (q, $^2J_{PtH}$ = 71.9 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, Pt-C$H_2$$CH_3$), 1.36 (s, $^2J_{PtH}$ = 71.0 Hz, 6H, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 7.85 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, $^tBu_2bpy$-H^5), 8.71 (s, $^4J_{HH}$ = 2 Hz, 2H, $^tBu_2bpy$-H^3), 8.86 (d, $^3J_{PtH}$ = 14 Hz, $^3J_{HH}$ = 6 Hz, 2H, $^tBu_2bpy$-H^6).

$PtIMe_2{}^iPr(^tBu_2bpy)$. This complex was prepared by the reaction of $PtMe_2(^tBu_2bpy)$ (104.5 mg, 0.2117 mmol) with ^{i}PrI (25.0 μl, 0.250 mmol). Yield: 101% (141.7 mg, 0.2136 mmol). ^1H NMR (C_6D_6, rt, 300 MHz): δ 0.43 (d, 6H, $^3J_{PtH}$ = 59.2 Hz, $^3J_{HH}$ = 7 Hz, Pt-CH(CH_3)$_2$), 0.94 (s, 18H, ^{t}Bu), 1.91 (septet, 1H, $^2J_{PtH}$ = 57.1 Hz, $^3J_{HH}$ = 7 Hz, Pt-CH(CH_3)$_2$), 2.12 (s, 6H, $^2J_{PtH}$ = 71.5 Hz, Pt-CH_3), 6.75 (dd, 2H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^tBu_2bpy$-H^5), 7.79 (d, 2H, $^4J_{HH}$ = 2 Hz, $^tBu_2bpy$-H^3), 8.75 (d, 2H, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, $^tBu_2bpy$-H^6).

$PtIMe_2Np(^tBu_2bpy)$. This complex was prepared by the reaction of $PtMe_2(^tBu_2bpy)$ (124.8 mg, 0.2529 mmol) with NpI (35.0 μl, 0.264 mmol) as pale-yellow powder in 98% (171.2 mg, 0.2475 mmol). ^1H NMR (acetone-d_6, rt, 400 MHz): δ 0.43 (brs, 9H, Pt-CH_2C(CH_3)$_3$), 1.45 (s, 6H, $^2J_{PtH}$ = 70.5 Hz, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 1.59 (s, 2H, $^2J_{PtH}$ = 72.3 Hz, Pt-CH_2C(CH_3)$_3$), 7.86 (dd, 2H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^tBu_2bpy$-H^5), 8.68 (d, 2H, $^4J_{HH}$ = 2 Hz, $^tBu_2bpy$-H^3), 8.96 (d, 2H, $^3J_{PtH}$ = 14 Hz, $^3J_{HH}$ = 6 Hz, $^tBu_2bpy$-H^6).

$PtIMe_2{}^n$Hex(^{t}Bu$_2$bpy). This complex was prepared by the reaction of $PtMe_2$(^{t}Bu$_2$bpy) (91.0 mg, 0.184 mmol) with ^{n}HexI (100 μl, 0.679 mmol) as pale-yellow powder in 97% (125.3 mg, 0.1776 mmol). ^{1}H NMR (acetone-d_6, 400 MHz, rt): δ 0.46 (m, 2H, Pt-$CH_2CH_2(CH_2)_3CH_3$), 0.69 (t, $^3J_{HH}$ = 7 Hz, 3H, Pt-$(CH_2)_5CH_3$), 0.85-1.05 (overlapped, 6H, Pt-$(CH_2)_2CH_2CH_2CH_2CH_3$), 1.3 (overlapped, 2H, Pt-$CH_2(CH_2)_4CH_3$), 1.38 (s, $^2J_{PtH}$ = 70.6 Hz, 6H, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 7.84 (dd, 2H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, ^{t}Bu$_2$bpy-H^5), 8.70 (d, 2H, $^4J_{HH}$ = 2 Hz, ^{t}Bu$_2$bpy-H^3), 8.87 (d, 2H, $^3J_{PtH}$ = 14 Hz, $^3J_{HH}$ = 6 Hz, ^{t}Bu$_2$bpy-H^6).

$PtIMe_2$Ph(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtMePh(^{t}Bu$_2$bpy) (202.4 mg, 0.3643 mmol) with MeI (500 μl, 8.03 mmol) in 93% (235.8 mg, 0.3380 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz, rt): δ 1.02 (s, $^2J_{PtH}$ = 71.9 Hz, 3H, Pt-CH_3 trans to I), 1.42 (s, 9H, ^{t}Bu), 1.46 (s, 9H, ^{t}Bu), 1.77 (s, $^2J_{PtH}$ = 70.1 Hz, 3H, Pt-CH_3 trans to N), 7.0-7.2 (m, 3H, $H_{m,p}$ of Ph), 7.47 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.64 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.7 (br, 2H, H_o of Ph), 8.13 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.15 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.79 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6), 8.93 (d, $^3J_{PtH}$ = 14 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6).

$PtIMe_2(C_6H_4OMe$-*p*)(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtMe(C_6H_4OMe-*p*)(^{t}Bu$_2$bpy) (155.1 mg, 0.2648 mmol) with MeI (500 μl, 8.03 mmol) as pale-yellow powder in 98% (188.0 mg, 0.2584 mmol). ^{1}H NMR (acetone-d_6, 400 MHz, rt): δ 0.93 (s, $^2J_{PtH}$ = 71.4 Hz, 3H, Pt-CH_3 trans to I), 1.46 (s, 9H, ^{t}Bu), 1.50 (s, 9H, ^{t}Bu), 1.66 (s, $^2J_{PtH}$ = 70.5 Hz, 3H, Pt-CH_3 trans to N), 3.76 (s, 3H, $C_6H_4OCH_3$-*p*), 6.68 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H_m of Ar), 7.55 (br, 2H, H_o of Ar), 7.76 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H$^{5'}$), 7.91 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 8.72 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H$^{6'}$), 8.74 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H$^{3'}$), 8.76 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.95 (d, $^3J_{PtH}$ = 14 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6).

Preparation of triorgano(nitorato)(4,4´-di-*tert*-butyl-2,2´-bipyridine)platinum.

These complexes were prepared according to the analogous literature methods with modifications.[1]

$Pt(NO_3)Me_2Et(bpy)$. This complex was prepared analogously by the reaction of $PtIMe_2Et(bpy)$ (73.8 mg, 0.137 mmol) with $AgNO_3$ (73.8 mg, 0.137 mmol) as white powder in 98% (63.7 mg, 0.135 mmol). *cis* isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, r.t.): δ 0.44 (s, $^2J_{PtH}$ = 80.1 Hz, 3H, Pt-CH_3 trans to NO_3), 0.96 (t, $^3J_{PtH}$ = 43.1 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-CH_2CH_3), 1.29 (s, $^2J_{PtH}$ = 66.9 Hz, 3H, Pt-CH_3 trans to N), 1.8-2.1 (m, 2H, Pt-C$H_2$$CH_3$), 7.66 (t, $^3J_{HH}$ = 6 Hz, 2H, bpy-$H^{5,5'}$), 8.08 (t, $^3J_{HH}$ = 8 Hz, 2H, bpy-$H^{4,4'}$), 8.19 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy-$H^{3,3'}$), 8.94 (d, $^3J_{PtH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, 2H, bpy-$H^{6,6'}$). *trans* isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, r.t.): δ 0.02 (t, $^2J_{PtH}$ = 67.8 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-CH_2CH_3), 1.25 (s, $^2J_{PtH}$ = 68.2 Hz, 6H, Pt-CH_3), 1.55 (q, $^2J_{PtH}$ = 78.3 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, Pt-C$H_2$$CH_3$), 7.66 (t, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^5), 8.08 (t, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^4), 8.19 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^3), 8.94 (d, $^3J_{PtH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^6).

$Pt(NO_3)Me_2Ph(bpy)$. This complex was prepared analogously by the reaction of $PtIMe_2Ph(bpy)$ (32.5 mg, 0.0555 mmol) with $AgNO_3$ (23.3 mg, 0.137 mmol) as white powder in 96% (27.8 mg, 0.0534mmol) (*cis*/*trans* = 2/1). *cis* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, r.t.): δ 0.92 (s, $^2J_{PtH}$ = 78.8 Hz, 3H, Pt-CH_3 trans to NO_3), 1.42 (s, $^3J_{PtH}$ = 66.8 Hz, 3H, Pt-CH_3 trans to N), 7.03-7.20 (m, 3H, $H_{m,p}$ of Ph), 7.37 (br, 2H, H_o of Ph), 7.79 (m, 1H, bpy-H^5), 7.97 (m, 1H, bpy-$H^{5'}$), 8.33 (m, 1H, bpy-H^4), 8.41 (m, 1H, bpy-$H^{4'}$), 8.6 (m, 1H, bpy-H^3), 8.74 (d, $^3J_{HH}$ = 9 Hz, 1H, bpy-H^6), 8.76 (d, $^3J_{HH}$ = 9 Hz, 1H, bpy-$H^{3'}$), 9.07 (d, $^3J_{HH}$ = 6 Hz, 1H, bpy-$H^{6'}$). *trans* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, r.t.): δ 1.50 (s, $^2J_{PtH}$ = 63.2 Hz, 6H, Pt-CH_3 (cis isomer)), 6.64-6.86 (m, 5H, Pt-*Ph*), 7.97 (m, 2H, bpy-H^5), 8.33 (m, 2H, bpy-H^4), 8.6 (m, 2H, bpy-H^3), 9.29 (d, $^3J_{HH}$ = 5 Hz, 2H, bpy-H^6).

$Pt(NO_3)Me_3(^tBu_2bpy)$. This complex was prepared analogously by the reaction of $PtIMe_3(^tBu_2bpy)$ (348.8 mg, 0.5489 mmol) with $AgNO_3$ (189.9 mg, 1.118 mmol) as white powder in 103% (322.8 mg, 0.5657 mmol). Anal. Calcd. for $C_{21}H_{33}N_3O_3Pt$: C, 44.20; H, 5.83; N, 7.36. Found: C, 44.30; H, 5.77; N, 6.86. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.53 (s, $^2J_{PtH}$ = 79.6 Hz, 3H, Pt-CH_3 trans to NO_3), 1.25 (s, $^2J_{PtH}$ = 66.7 Hz, 6H, Pt-CH_3 trans to N), 1.44 (s, 18H, ^{t}Bu), 7.62 (dd,

$^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.10 (d, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^3), 8.81 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$Et(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe$_2$Et(^{t}Bu$_2$bpy) (95.4 mg, 0.147 mmol)with AgNO$_3$ (66.5 mg, 0.391 mmol) as white powder in 103% (322.8 mg, 0.5657 mmol). (*cis* / *trans* = 1 / 4). Anal. Calcd. for $C_{22}H_{35}N_3O_3Pt$: C, 45.20; H, 6.03; N, 7.19. Found: C, 45.18; H, 6.42; N, 6.86. *Cis* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, rt): δ 0.05 (t, $^2J_{PtH}$ = 66.0 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-CH$_2$CH_3), 1.14 (s, $^2J_{PtH}$ = 68.2 Hz, 6H, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 1.5 (overlapped, Pt-CH_2CH$_3$), 7.89 (d, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.72 (s, 2H, ^{t}Bu$_2$bpy-H^3), 8.87 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6). *Trans* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, rt): δ 0.40 (s, $^2J_{PtH}$ = 79.7 Hz, 3H, Pt-CH_3 trans to NO$_3$), 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 3H, Pt-CH$_2$CH_3), 1.18 (s, 3H, Pt-CH_3 trans to N), 1.48 (s, 18H, ^{t}Bu), 7.89 (d, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.72 (s, 2H, ^{t}Bu$_2$bpy-H^3), 8.87 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$^{i}Pr(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe^{i}Pr$_2$(^{t}Bu$_2$bpy) (123.0 mg, 0.1854 mmol) with AgNO$_3$ (143.6 mg, 0.8454 mmol) as white powder in 108% (120.1 mg, 0.201 mmol). ^{1}H NMR (acetone-d_6, rt, 400 MHz): δ 0.27 (d, $^3J_{PtH}$ = 60.4 Hz, $^3J_{HH}$ = 7 Hz, 6H, Pt-CH(CH_3)$_2$), 1.19 (s, $^2J_{PtH}$ = 69.2 Hz, 6H, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 2.13 (septet, $^3J_{HH}$ = 7 Hz, 1H, Pt-CH(CH$_3$)$_2$), 7.88 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.71 (d, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^3), 8.92 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$Np(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe$_2$Np(^{t}Bu$_2$bpy) (253.1 mg, 0.3660 mmol) with AgNO$_3$ (135.2 mg, 0.7959 mmol) as white powder in 92% (211.4 mg, 0.3373 mmol). Anal. Calcd. for $C_{25}H_{41}N_3O_3Pt$: C, 47.91; H, 6.59; N, 6.71. Found: C, 47.92; H, 6.55; N, 6.73. *Cis* isomer: ^{1}H NMR (C_6D_6, 400 MHz, rt): δ 0.64 (s, $^2J_{PtH}$ = 67.8 Hz, 3H, Pt-CH_3 trans to NO$_3$), 0.98 (s, 9H, ^{t}Bu), 1.02 (s, 9H, ^{t}Bu), 1.59 (s, 9H, Pt-CH$_2$C(CH_3)$_3$), 1.86 (s, $^2J_{PtH}$ = 66.8 Hz, 3H, Pt-CH_3 trans to N), 2.1-2.4 (m, 2H, Pt-CH_2C(CH$_3$)$_3$), 6.75 (d, $^3J_{HH}$ = 4 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 6.76 (d, $^3J_{HH}$ = 4 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 8.21 (s, 1H, ^{t}Bu$_2$bpy-H^3), 8.25 (s, 1H, ^{t}Bu$_2$bpy-H^3), 8.51 (d, $^3J_{PtH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6), 8.81 (d, $^3J_{PtH}$ =

11 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6). *Trans* isomer: ^{1}H NMR (C_6D_6, 400 MHz, rt): δ 0.58 (brs, 9H, Pt-CH$_2$C(C*H*$_3$)$_3$), 0.98 (s, 18H, ^{t}Bu), 1.77 (s, $^2J_{PtH}$ = 67.8 Hz, 6H, Pt-C*H*$_3$), 1.98 (s, $^2J_{PtH}$ = 78.8 Hz, 2H, Pt-C*H*$_2$C(CH$_3$)$_3$), 6.86 (d, $^3J_{HH}$ = 5 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.15 (d, $^4J_{HH}$ = 1 Hz, 2H, ^{t}Bu$_2$bpy-H^3), 8.63 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$(^{n}Hex)(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe$_2$^{n}Hex(^{t}Bu$_2$bpy) (120.5 mg, 0.1708 mmol) with AgNO$_3$ (68.4 mg, 0.403 mmol) as white powder in 91% (100.0 mg, 0.1561 mmol). Anal. Calcd. for $C_{25}H_{41}N_3O_3Pt$: C, 47.91; H, 6.59; N, 6.71. Found: C, 47.92; H, 6.55; N, 6.73. *T*rans isomer: ^{1}H NMR (acetone-*d*$_6$, 400 MHz, rt): δ 0.49 (br, 2H, Pt-CH$_2$C*H*$_2$(CH$_2$)$_3$CH$_3$), 0.67 (t, $^3J_{HH}$ = 7 Hz, 3H, Pt-(CH$_2$)$_5$C*H*$_3$), other ^{n}Hex protons were not determined, 1.00 (s, 18H, ^{t}Bu), 1.74 (s, $^2J_{PtH}$ = 67.3 Hz, 6H, Pt-C*H*$_3$), 6.87 (brs, 2H, ^{t}Bu$_2$bpy-H^5), 8.12 (brs, 2H, ^{t}Bu$_2$bpy-H^3), 8.63 (brd, 2H, $^3J_{HH}$ = 6 Hz, ^{t}Bu$_2$bpy-H^6). *Ci*s isomer: ^{1}H NMR (acetone-*d*$_6$, 400 MHz, rt): δ 1.00 (s, 18H, ^{t}Bu), 6.80 (br, 2H, ^{t}Bu$_2$bpy-H^5), 8.07 (br, 2H, ^{t}Bu$_2$bpy-H^3), 8.58 (brd, 1H, $^3J_{HH}$ = 5 Hz, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$Ph(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe$_2$^{n}Hex(^{t}Bu$_2$bpy) (106.1 mg, 0.1521 mmol) with AgNO$_3$ (67.2 mg, 0.396 mmol) as white powder in 93% (89.6 mg, 0.142 mmol) (*cis*/*trans* = 2/1). Anal. Calcd. for $C_{26}H_{35}N_3O_3Pt$: C, 49.36; H, 5.58; N, 6.64. Found: C, 48.98; H, 5.63; N, 6.64. *cis* isomer: ^{1}H NMR (acetone-*d*$_6$, 400 MHz, rt): δ 0.88 (s, $^2J_{PtH}$ = 78.8 Hz, 3H, Pt-C*H*$_3$ *trans* to NO$_3$), 1.39 (s, $^2J_{PtH}$ = 66.8 Hz, 3H, Pt-C*H*$_3$ *trans* to N), 1.45 (s, 9H, ^{t}Bu), 1.50 (s, 9H, ^{t}Bu), 7.05-7.18 (m, 3H, H$_{m,p}$ of Ph), 7.02-7.70 (br, 2H, H$_o$ of Ph), 7.79 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.96 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H$^{5'}$), 8.48 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz 1H, ^{t}Bu$_2$bpy-H^6), 8.76 (d, $^4J_{HH}$ = 1 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.78 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H$^{3'}$), 8.93 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H$^{6'}$). *trans* isomer: ^{1}H NMR (acetone-*d*$_6$, 400 MHz, rt): δ 1.45 (s, 18H, ^{t}Bu), 1.46 (s, $^2J_{PtH}$ = 66.9 Hz, 6H, Pt-C*H*$_3$ *trans* to N), 6.65-6.88 (m, 5H Pt-*Ph*), 7.96 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 8.62 (d, $^4J_{HH}$ = 2 Hz, ^{t}Bu$_2$bpy-H^3), 9.16 (d, $^3J_{PtH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, ^{t}Bu$_2$bpy-H^6).

Pt(NO$_3$)Me$_2$(C$_6$H$_4$OMe-*p*)(^{t}Bu$_2$bpy). This complex was prepared analogously by the reaction of PtIMe$_2$(C$_6$H$_4$OMe-*p*)(^{t}Bu$_2$bpy) (152.0 mg, 0.2089 mmol) with AgNO$_3$ (91.0 mg, 0.536 mmol) as yellow-white powder in 95% (132.1 mg, 0.1993 mmol) (*cis*/*trans* = 2/1). Anal. Calcd. for C$_{27}$H$_{37}$N$_3$O$_4$Pt: C, 48.94; H, 5.63; N, 6.34. Found: C, 48.88; H, 5.73; N, 6.28. *Cis* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, r.t.): δ 0.86 (s, $^2J_{PtH}$ = 78.8 Hz, 3H, Pt-CH_3 trans to NO$_3$), 1.37 (s, $^2J_{PtH}$ = 66.0 Hz, 3H, Pt-CH_3 trans to N), 1.45 (s, 9H, ^{t}Bu), 1.49 (s, 9H, ^{t}Bu), 3.79 (s, 3H, O*Me*), 6.79 (m, 2H, H^m of Ar), 7.23 (br, 2H, H^o of Ar), 7.79 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.95 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 8.48 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6), 8.75 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.78 (d, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.92 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6). *Trans* isomer: ^{1}H NMR (acetone-d_6, 400 MHz, r.t.): δ 1.44 (s, $^2J_{PtH}$ = 66.9 Hz, 6H, Pt-CH_3), 1.45 (s, 18H, ^{t}Bu), 3.56 (s, 3H, O*Me*), 6.35 (m, 2H, H^m of Ar), 6.64 (m, 2H, H^o of Ar), 7.95 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.63 (d, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^3), 9.13 (d, $^3J_{PtH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

PtMeAr(^{t}Bu$_2$bpy) (Ar = Ph, C$_6$H$_5$OMe-p). Thes complexes was prepared analogously by the reaction of PtMeAr(cod) with ^{t}Bu$_2$bpy. Yield: 72% (244.0 mg, 0.4392 mmol). Anal. Calcd. for C$_{25}$H$_{32}$N$_2$Pt: C, 54.04; H, 5.81; N, 5.04. Found: C, 53.66; H, 5.87; N, 4.88. ^{1}H NMR (CDCl$_3$, 400 MHz, rt): δ 1.14 (s, $^3J_{PtH}$ = 85.2 Hz, 3H, Pt-CH_3), 1.37 (s, 9H, ^{t}Bu), 1.42 (s, 9H, ^{t}Bu), 6.95 (tt, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, H$_p$ of Ph), 7.10 (t, $^3J_{HH}$ = 7 Hz, 2H, H$_m$ of Ph), 7.34 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.49 (dd, $^3J_{PtH}$ = 65.0 Hz, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 2H, H$_o$ of Ph), 7.52 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5), 7.91 (d, $^4J_{HH}$ = 1 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 7.95 (d, $^4J_{HH}$ = 1 Hz, 1H, ^{t}Bu$_2$bpy-H^3), 8.58 (d, $^3J_{PtH}$ = 21.0 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6), 9.07 (d, $^3J_{PtH}$ = 18.7 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6).

PtMe(C$_6$H$_4$OMe-*p*)(^{t}Bu$_2$bpy)

Yield: 76% (209.1 mg, 0.3570 mmol). Anal. Calcd. for C$_{26}$H$_{34}$N$_2$OPt: C, 53.32; H, 5.85; N, 4.78. Found: C, 53.62; H, 5.75; N, 4.71. ^{1}H NMR (C$_6$D$_6$, 400 MHz, r.t.): δ 0.91 (s, 9H, ^{t}Bu), 0.96 (s, 9H,

^{t}Bu), 2.05 (s, $^2J_{PtH}$ = 86.6 Hz, 3H, Pt-CH_3), 3.66 (s, 3H, OCH_3), 6.32 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5 trans to Ar), 6.60 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, ^{t}Bu$_2$bpy-H^5 trans to Me), 7.25 (d, $^3J_{HH}$ = 8 Hz, 2H, H$_m$ of Ar), 7.42 (d, $^4J_{HH}$ = 1 Hz, 1H, ^{t}Bu$_2$bpy-H^3 trans to Ar), 7.47 (d, $^4J_{HH}$ = 1 Hz, 1H, ^{t}Bu$_2$bpy-H^3 trans to Me), 8.14 (d, $^3J_{PtH}$ = 63.6 Hz, $^3J_{HH}$ = 9 Hz, 2H, H$_o$ of Ar), 8.83 (d, $^3J_{PtH}$ = 30.7 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6 trans to Ar), 9.07 (d, $^3J_{PtH}$ = 31.1 Hz, $^3J_{HH}$ = 6 Hz, 1H, ^{t}Bu$_2$bpy-H^6 trans to Me).

Preparation of (2,2´-bipyridine) or (4,4´-di-*tert*-butyl-2,2´-bipyridine)triorganoplatinum-manganesepentacarbonyl complexes. A typical procedure for (bpy)Me$_3$Pt–Mn(CO)$_5$ (**1a**) is given. To a THF solution of PtMe$_3$NO$_3$(bpy) (100.6 mg, 0.2195 mmol 198.2 mg, 0.308 mmol), a THF solution of Na[Mn(CO)$_5$] (73.8 mg, 0.339 mmol) was added at -30°C and the mixture stirred for 6 h. The resulting solution was evaporated to dryness and the resulting red-purple solids extracted with toluene. After the filtered solution was concentrated under reduced pressure, the solution was cooled to −20 °C to give dark-red prisms. Yield: 54% (70.0 mg, 0.118 mmol). Anal. Calcd. for $C_{18}H_{17}N_2O_5MnPt$: C, 36.56; H, 2.90; N, 4.74. Found: C, 36.49; H, 2.99; N, 4.73. m.p., 125 °C (dec.). Molar Electric Conductivity Λ: 0.513 S cm^2 mol^{-1} (THF, rt), 17 S cm^2 mol^{-1} (in acetone at r.t.). UV-vis. (THF): 299, 309, 325 (sh), 533 nm. IR (ν_{CO}, KBr): 2031, 1957, 1935, 1909, 1887 cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz, rt): δ 0.50 (s, $^2J_{PtH}$ = 67.3 Hz, 3H, Pt-CH_3 trans to Mn), 1.78 (s, $^2J_{PtH}$ = 70.6 Hz, 6H, Pt-CH_3 trans to N), 6.48 (t, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^5), 6.76 (t, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^4), 7.08 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^3), 8.75 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^6).

(bpy)Me$_2$EtPt–Mn(CO)$_5$ (1b). Complex **1b** was prepared analogously to **1a** by the reaction of PtMe$_2$Et(NO$_3$)(bpy) (30.4 mg, 0.0664 mmol) with Na[Mn(CO)$_5$] (36.1 mg, 0.166 mmol) as purple powder in 91% (35.3 mg, 0.0583 mmol) from benzene/hexane. Anal. Calcd. for $C_{19}H_{19}N_2O_5MnPt$: C, 37.7; H, 3.16; N, 4.63. Found: C, 37.70; H, 3.16; N, 4.63. UV-vis. (in THF): 299, 310, 327 (sh), 543 nm. IR (ν_{CO}, KBr): 2028, 1949, 1935, 1908, 1888 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz, rt): δ -0.01 (t, $^3J_{PtH}$ = 71.9 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, Pt-CH$_2$CH_3), 1.18 (q, $^2J_{PtH}$ = 67.3 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, Pt-

CH_2CH_3), 1.66 (s, $^2J_{PtH}$ = 70.5 Hz, 6H, Pt-CH_3), 6.51 (t, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^5), 6.78 (t, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^4), 7.10 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^3), 8.69 (d, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^6).

(bpy)Me_2PhPt–Mn(CO)$_5$ (1c). Complex **1c** was prepared analogously to **1a** by the reaction of $PtMe_2Ph(NO_3)$(bpy) (60.5 mg, 0.116 mmol) with Na[Mn(CO)$_5$] (42.8 mg, 0.196 mmol) as red-purple powder in 55% (41.4 mg, 0.0634 mmol) from CH_2Cl_2/hexane. Anal. Calcd. for $C_{23}H_{19}N_2O_5MnPt$: C, 41.83; H, 3.14; N, 4.22. Found: C, 42.28; H, 2.93; N, 4.29. UV-vis (in THF): 300, 309, 326 (sh), 503 nm. IR (ν_{CO}, KBr): 2037, 1976, 1927, 1916 cm^{-1}. ^{1}H NMR (acetone-d_6, 300 MHz, -60 °C): δ 1.53 (s, $^2J_{PtH}$ = 70.3 Hz, 6H, Pt-CH_3), 6.6-6.9 (m, 5H, Pt-*Ph*), 6.48 (t, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^5), 6.76 (t, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^4), 8.68 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy-H^3), 9.43 (d, $^3J_{PtH}$ = 10 Hz, $^3J_{HH}$ = 6 Hz, 2H, bpy-H^6).

(^{t}Bu$_2$bpy)Me_3Pt–Mn(CO)$_5$ (2a). Complex **2a** was prepared analogously to **1a** by the reaction of $PtMe_3(NO_3)$(^{t}Bu$_2$bpy) (84.8 mg, 0.149 mmol) with Na[Mn(CO)$_5$] (46.2 mg, 0.212 mmol) as red-purple prisms in 53% (55.5 mg, 0.0789 mmol) from THF/hexane. Anal. Calcd. for $C_{26}H_{33}N_2O_5MnPt$: C, 44.39; H, 4.73; N, 3.98. Found: C, 44.18; H, 4.86; N, 4.00. UV-vis. (in THF): 299 (ε = 26000 L mol^{-1} cm^{-1}), 323 (ε = 16000 L mol^{-1} cm^{-1}, sh), 500 (ε = 3800 L mol^{-1} cm^{-1}). IR (ν_{CO}, KBr): 2033 (s), 1951 (sh), 1909 (vs) cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz, rt): δ 0.66 (s, $^2J_{PtH}$ = 67.8 Hz, 3H, Pt-CH_3 trans to Mn), 0.93 (s, 18H, ^{t}Bu), 0.66 (s, $^2J_{PtH}$ = 70.5 Hz, 6H, Pt-CH_3 trans to N), 6.73 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 7.99 (d, $^4J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^3), 8.84 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

(^{t}Bu$_2$bpy)Me_2EtPt–Mn(CO)$_5$ (2b). Complex **2b** was prepared analogously to **1a** by the reaction of $PtMe_2Et(NO_3)$(^{t}Bu$_2$bpy) (59.7 mg, 0.102 mmol) with Na[Mn(CO)$_5$] (54.6 mg, 0.250 mmol) as purple powder in 32% (23.3 mg, 0.0325 mmol) from benzene/hexane. Yield: 32% (23.3 mg, 0.0325 mmol). UV-vis. (in THF): 296, 308, 323 (sh), 507. IR (ν_{CO}, KBr): 2029 (m), 1932 (s, sh), 1907 (vs) cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz, rt): δ 0.16 (t, $^3J_{PtH}$ = 72.4 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-CH$_2$CH_3), 0.94 (s, 18H, ^{t}Bu), 1.32 (q, $^2J_{PtH}$ = 67.8 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, Pt-CH_2CH$_3$), 1.80 (s, $^2J_{PtH}$

= 70.1 Hz, 6H, Pt-CH_3), 6.77 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.05 (s, 2H, ^{t}Bu$_2$bpy-H^3), 8.79 (d, $^3J_{PtH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

(^{t}Bu$_2$bpy)Me$_2$^{i}PrPt–Mn(CO)$_5$ (2c). Complex **2c** was prepared analogously to **1a** by the reaction of PtMe$_2$^{i}Pr(NO$_3$)(^{t}Bu$_2$bpy) (48.6 mg, 0.0812 mmol) with Na[Mn(CO)$_5$] (30.3 mg, 0.139 mmol) as orange powder in 47% (27.7 mg, 0.0379 mmol) from CH_2Cl_2/hexane. Anal. Calcd. for $C_{28}H_{37}N_2O_5MnPt$: C, 45.97; H, 5.10; N, 3.83. Found: C, 44.53; H, 4.60; N, 3.92. UV-vis. (in THF): 253, 298, 309, 337, 537. IR (ν_{CO}, KBr): 2029 (m), 1945 (m, sh), 1909 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz, rt): δ 0.12 (d, $^3J_{PtH}$ = 68.7 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, Pt-CH(CH_3)$_2$), 1.20 (s, $^2J_{PtH}$ = 70.5 Hz, 6H, Pt-CH_3), 1.45 (s, 18H, ^{t}Bu), 7.59 (d, $^3J_{HH}$ = 5 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.22 (s, 2H, ^{t}Bu$_2$bpy-H^3), 8.82 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6), The α-methyne protone of ^{i}Pr group was not determined.

(^{t}Bu$_2$bpy)Me$_2$NpPt–Mn(CO)$_5$ (2d). Complex **2d** was prepared analogously to **1a** by the reaction of PtMe$_2$Np(NO$_3$)(^{t}Bu$_2$bpy) (58.3 mg, 0.0930 mmol) with Na[Mn(CO)$_5$] (28.9 mg, 0.133 mmol) as orange powder in 41% (41.3 mg, 0.0544 mmol)**.**from CH_2Cl_2/hexane. Anal. Calcd. for $C_{30}H_{41}N_2O_5MnPt$: C, 47.43; H, 5.44; N, 3.69. Found: C, 47.47; H, 5.43; N, 3.63. UV-vis. (in THF): 251, 298, 307, 346, 536. IR (ν_{CO}, KBr): 2028 (s), 1949 (s, sh), 1909 (vs) cm^{-1}. ^{1}H NMR (acetone-*d*$_6$, 400 MHz, rt): δ 0.48 (s, 9H, PtCH$_2$C(CH_3)$_3$), 1.30 (s, $^3J_{PtH}$ = 69.1 Hz, 6H, Pt-CH_3), 1.48 (s, 18H, ^{t}Bu), 7.98 (d, $^3J_{HH}$ = 5 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.82 (s, 2H, ^{t}Bu$_2$bpy-H^3), 9.03 (d, $^3J_{PtH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6), The α-methylene protones of Np group was not determined.

(^{t}Bu$_2$bpy)Me$_2$^{n}HexPt–Mn(CO)$_5$ (2e). Complex **2e** was prepared analogously to **1a** by the reaction of PtMe$_2$^{n}Hex(NO$_3$)(^{t}Bu$_2$bpy) (45.6 mg, 0.712 mmol) with Na[Mn(CO)$_5$] (21.2 mg, 0.09730mmol) as orange powder in 76% (42.1 mg, 0.0544 mmol) from toluene/hexane. Anal. Calcd. for $C_{31}H_{43}N_2O_5MnPt$: C, 48.12; H, 5.60; N, 3.62. Found: C, 47.81; H, 5.25; N, 3.64. UV-vis. (in THF): 252, 296, 307, 327 (sh), 525. IR (ν_{CO}, KBr): 2029 (s), 1949 (m, sh), 1916 (vs), 1898 (vs) cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz, rt): δ 0.48 (quint, $^3J_{HH}$ = 8 Hz, 2H, Pt-CH$_2$CH_3(CH$_2$)$_3$CH$_3$), 0.66 (t, $^3J_{HH}$ = 7 Hz, 3H, Pt-(CH$_2$)$_5$CH_3), 0.8-1.0 (overlapped, Pt-(CH$_2$)$_2$CH_2CH_2CH_2CH$_3$), 0.95 (s, 18H, ^{t}Bu), 1.35

(tt, $^{2}J_{PtH}$ = 68 Hz, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 8 Hz, 2H, Pt-CH_2(CH$_2$)$_4$CH$_3$), 1.84 (s, $^{2}J_{PtH}$ = 70.1 Hz, 6H, Pt-CH_3), 6.80 (d, $^{3}J_{HH}$ = 5 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 8.09 (s, 2H, ^{t}Bu$_2$bpy-H^3), 8.84 (d, $^{3}J_{PtH}$ = 13 Hz, $^{3}J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

(^{t}Bu$_2$bpy)Me$_2$PhPt–Mn(CO)$_5$ (2f). Complex **2f** was prepared analogously to **1a** by the reaction of PtMe$_2$Ph(NO$_3$)(^{t}Bu$_2$bpy) (54.4 mg, 0.0860 mmol) with Na[Mn(CO)$_5$] (40.9 mg, 0.188 mmol) as orange powder in 81% (53.6 mg, 0.0700 mmol) from CH$_2$Cl$_2$/hexane. Anal. Calcd. for $C_{30}H_{17}N_2O_5MnPt$: C, 48.63; H, 4.61; N, 3.66. Found: C, 48.41; H, 5.14; N, 3.72. UV-vis. (in THF): 298, 308, 327 (sh), 474. IR (ν_{CO}, KBr): 2035 (m), 1927 (vs) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz, rt): δ 0.88 (s, 18H, ^{t}Bu), 2.18 (s, $^{2}J_{PtH}$ = 70.5 Hz, 6H, Pt-CH_3), 6.71 (d, $^{3}J_{HH}$ = 7 Hz, 1H, H$_p$ of Ph), 6.83 (t, $^{3}J_{HH}$ = 7 Hz, 2H, H$_m$ of Ph), 6.90 (dd, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 7.01 (d, $^{3}J_{PtH}$ = 53 Hz, $^{3}J_{HH}$ = 7 Hz, 2H, H$_o$ of Ph), 7.72 (d, 2H, ^{t}Bu$_2$bpy-H^3), 9.09 (d, $^{3}J_{PtH}$ = 12 Hz, $^{3}J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

(^{t}Bu$_2$bpy)Me$_2$(*p*-MeOC$_6$H$_4$)Pt–Mn(CO)$_5$ (2g). Complex **2g** was prepared analogously to **1a** by the reaction of PtMe$_2$(C$_6$H$_4$OMe-*p*)(NO$_3$)(^{t}Bu$_2$bpy) (39.4 mg, 0.0595 mmol) with Na[Mn(CO)$_5$] (22.9 mg, 0.105 mmol) as orange powder in 43% (20.5 mg, 0.0258 mmol) from toluene/hexane. Yield: 43% (20.5 mg, 0.0258 mmol). IR (ν_{CO}, KBr): 2035 (m), 1923 (vs) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz, rt): δ 0.89 (s, 18H, ^{t}Bu), 2.19 (s, $^{2}J_{PtH}$ = 70.5 Hz, 6H, Pt-CH_3), 3.10 (s, 3H, C6H4O*Me-p*), 6.47 (d, $^{3}J_{HH}$ = 8 Hz, 2H, H$_m$ of Ar), 6.86 (d, $^{3}J_{PtH}$ = 54 Hz, $^{3}J_{HH}$ = 8 Hz, 2H, H$_o$ of Ar), 6.92 (d, $^{3}J_{HH}$ = 5 Hz, 2H, ^{t}Bu$_2$bpy-H^5), 7.76 (s, 2H, ^{t}Bu$_2$bpy-H^3), 9.11 (d, $^{3}J_{PtH}$ = 11 Hz, $^{3}J_{HH}$ = 6 Hz, 2H, ^{t}Bu$_2$bpy-H^6).

UV-vis Spectrum of (2,2´-bipyridine) or (4,4´-di-*tert*-butylbipyridine)triorganoplatinum-manganesepentacarbonyl complexes.

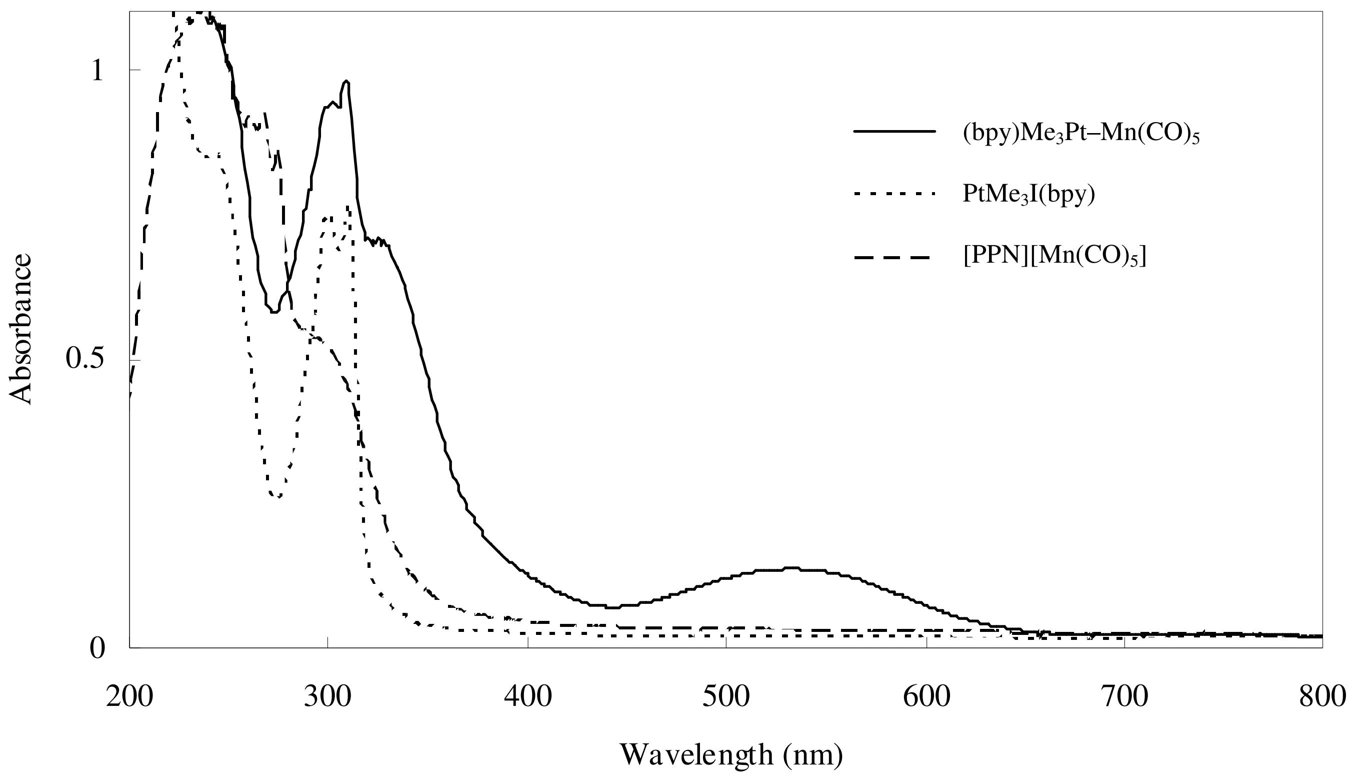

Figure S1. UV-vis. Spectrum of (bpy)Me_3Pt–$Mn(CO)_5$ (**1a**), $PtIMe_3$(bpy) and [PPN][$Mn(CO)_5$].

Table S1. Wavelength of Maximum Absorption of (bpy)Me_2RPt–$Mn(CO)_5$ and ($^t Bu_2$bpy)Me_2RPt–$Mn(CO)_5$ in THF

Run	Complex	solvent	MLCT band (nm)
1	**1a**	THF	523, 325
2	**1b**	THF	543, 327
3	**1c**	THF	503, 326
4	**2a**	THF	500, 323
5	**2b**	THF	507, 323
6	**2c**	THF	537, 337
7	**2d**	THF	536, 346
8	**2e**	THF	525, 327
9	**2f**	THF	474, 327
10	**2f**	benzene	546, 323
11	**2f**	acetone	446, 320

X-ray Structure Analyses of (bpy)Me_3Pt–$Mn(CO)_5$ (1a)

The crystallographic data were measured on a Rigaku RASA-7R four-circle diffractometer using MoKα (λ = 0.71069 Å) radiation with a graphite crystal monochromator at -73 °C. Intensity data were collected using the ω-2θ technique to a maximum 2θ of 54.9°. Intensities were corrected for Lorentz and polarization effects. An absorption correction for **1a** was applied with the program PSI SCAN method. The structure of **1a** was solved by Patterson methods[4] and expanded using Fourier techniques.[5] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All hydrogen atoms were added geometrically and refined by using a riding model. All calculations were performed using the *CrystalStructure* 3.82[6] crystallographic software package except for refinement, which was performed using SHELXL-97[7] The crystallographic data and selected bond distances and angles are summarized in Tables S2 and S3, respectively.

Table S2. Crystallographic data for (bpy)Me_3Pt-Mn$(CO)_5$ (**1a**).

Empirical formula	$C_{18}H_{17}N_2O_5PtMn$
Formula weight	591.37
Crystal color, habit	dark red, prismatic
Crystal dimension (mm × mm × mm)	0.46×0.13×0.10
Crystal system	monoclinic
Space Group	$P2_1$/a (No. 14)
a (Å)	13.574(3)
b (Å)	10.5780(17)
c (Å)	13.601(3)
β (°)	103.415(14)
V (Å^3)	1899.6(6)
Z	4
D_{calcd} (g cm^{-3})	2.068
F_{000}	1128.00
μ (Mo Kα) (cm^{-1})	80.226
Diffractometer	Rigaku AFC7R
Radiation (Å)	0.71069
Temperature (°C)	-73 °C
Scan Type	ω-2θ
$2\theta_{max}$ (°)	54.9
No. of Reflection Measured	Total: 4523
	Unique: 4340
Structure Solution	Patterson Methods (DIRDIF99 PATTY)
R_1[a] (I>2.00σ(I))	0.0292
wR_2[b] (All reflections)	0.0816
Goodness of Fit Indicator	0.936

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table S3. Selected Bond Lengths (Å) and Selected Bond Angles (deg.) of (bpy)Me_3Pt-Mn$(CO)_5$ (**1a**)

Pt(1)-Mn(1)	3.0337(8)	Pt(1)-N(1)	2.156(5)
Pt(1)-N(2)	2.166(4)	Pt(1)-C(1)	2.076(6)
Pt(1)-C(2)	2.057(5)	Pt(1)-C(3)	2.055(5)
Mn(1)-C(14)	1.845(5)	Mn(1)-C(15)	1.813(5)
Mn(1)-C(16)	1.828(4)	Mn(1)-C(17)	1.832(4)
Mn(1)-C(18)	1.797(5)	C(14)-O(1)	1.136 (7)
C(15)-O(2)	1.153(6)	C(16)-O(3)	1.148(6)
C(17)-O(4)	1.150(6)	C(18)-O(5)	1.153(9)
Mn(1)-Pt(1)-N(1)	92.71(12)	Mn(1)-Pt(1)-N(2)	89.87(12)
Mn(1)-Pt(1)-C(1)	178.28(14)	Mn(1)-Pt(1)-C(2)	94.30(18)
Mn(1)-Pt(1)-C(3)	94.13(18)	N(1)-Pt(1)-N(2)	76.51(14)
N(1)-Pt(1)-C(1)	86.03(18)	N(1)-Pt(1)-C(2)	97.79(17)
N(1)-Pt(1)-C(3)	173.0(2)	N(2)-Pt(1)-C(1)	88.7(2)
N(2)-Pt(1)-C(2)	173.12(18)	N(2)-Pt(1)-C(3)	99.27(19)
C(1)-Pt(1)-C(2)	87.0(2)	C(1)-Pt(1)-C(3)	87.0(2)
C(2)-Pt(1)-C(3)	85.9(2)	Pt(1)-Mn(1)-C(14)	82.0(2)
Pt(1)-Mn(1)-C(15)	77.87(18)	Pt(1)-Mn(1)-C(16)	85.56(17)
Pt(1)-Mn(1)-C(17)	79.63(17)	Pt(1)-Mn(1)-C(18)	178.89(15)
C(14)-Mn(1)-C(15)	87.5(2)	C(14)-Mn(1)-C(16)	167.6(2)
C(14)-Mn(1)-C(17)	88.6(2)	C(14)-Mn(1)-C(18)	98.1(2)
C(15)-Mn(1)-C(16)	89.2(2)	C(15)-Mn(1)-C(17)	157.5(2)
C(15)-Mn(1)-C(18)	101.0(2)	C(16)-Mn(1)-C(17)	89.8(2)
C(16)-Mn(1)-C(18)	94.3(2)	C(17)-Mn(1)-C(18)	101.5(2)
Mn(1)-C(14)-O(1)	177.8(5)	Mn(1)-C(15)-O(2)	177.0(5)
Mn(1)-C(16)-O(3)	178.1(4)	Mn(1)-C(17)-O(4)	178.2(5)
Mn(1)-C(18)-O(5)	178.4(4)		

Observed Rate Constant for the Methyl Transfer of 2f under Dark

Complex **2f** (ca. 1 mg, 0.001 mmol) was placed in a Schlenk type quartz UV cell and then 4.0 mL of solvent was added into the Schlenk tube by trap-to-trap transfer under reduced pressure. The time-course of the reaction was monitored by the absorption maximum at 535 nm. During measurement of the reaction, the temperature was set up at 20.0 °C by a thermostatted UV cell holder and the deviation of the temperature was less than ±0.5 °C.

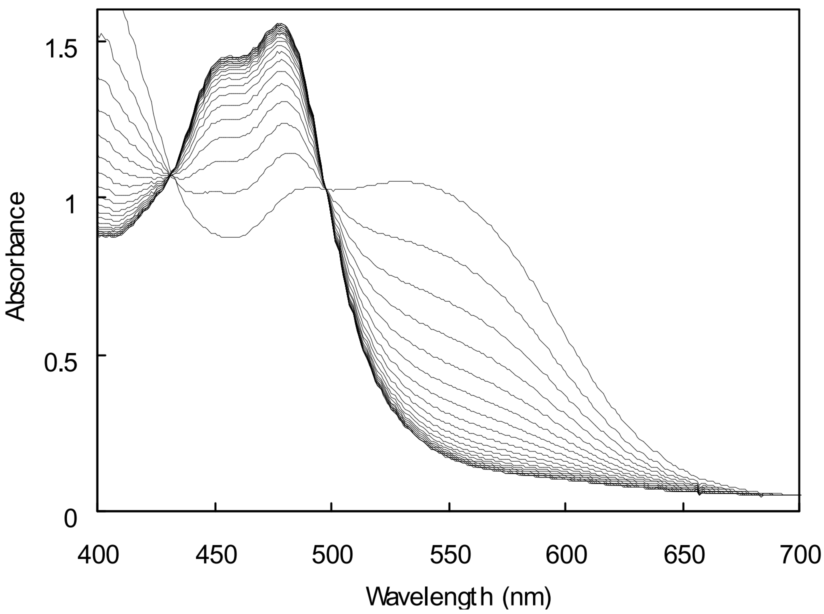

Figure S2. UV-vis spectral change for **2f**. Conditions: Solvent, benzene; temperature, 20 °C; under dark.

Table S4. First-order rate constants for the methyl transfer under dark

Entry	Complex	Solvent	Temperature (°C)	10^4 k_{obs} (s^{-1})
1	**2f**	benzene	15.0	0.768±0.001
2			20.0	1.63±0.003
3		THF	15.0	1.16±0.002
4		acetone	15.0	0.832±0.002
5	**2g**	benzene	20.0	1.57±0.005

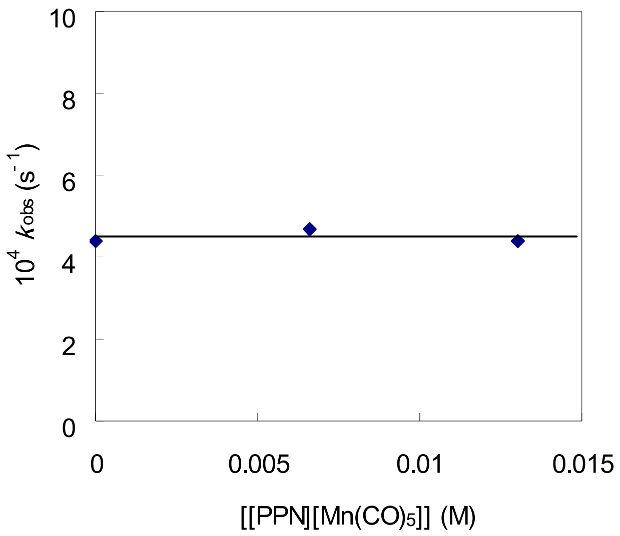

Figure S3. Effect of added $[PPN][Mn(CO)_5]$ on k_{obs} for $(^tBu_2bpy)Me_3Pt–Mn(CO)_5$ (**2f**). Conditions: Solvent, THF; temperature, 25 ℃; [**2f**] = 0.3 mM; under dark.

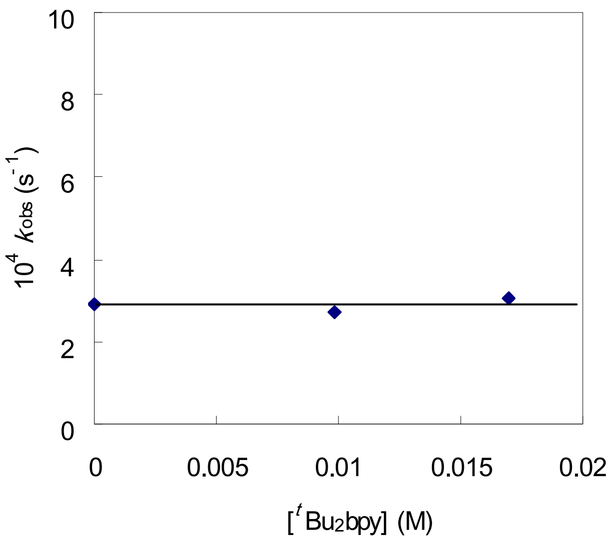

Figure S4. Effect of added $^tBu_2bpy$ on k_{obs} for $(^tBu_2bpy)Me_3Pt–Mn(CO)_5$ (**2f**). Conditions: Solvent, benzene; temperature, 25 ℃; [**9f**] = 0.3 mM; under dark.

Observed Rate Constant for the Methyl Transfer of 2f under Irradiation

Complex **2f** (ca. 1 mg, 0.001 mmol) was placed in a Schlenk type quartz UV cell and then 4.0 mL of solvent was added into the Schlenk tube by trap-to-trap transfer under reduced pressure. The solution of **2f** was photoirradiated with visible light of a super high-pressure UV lamp (500W, USIO Inc., Japan) equipped with a Y-50 sharp cut filter and HA-50 heat absorbing filter to cut off UV light and heat. The time-course of the reaction was monitored by the absorption maximum. During irradiation and measurement of the reaction, the temperature was set up at 15.0 or 20.0 °C by a thermostatted UV cell holder and the deviation of the temperature was less than ±0.5 °C. The solution of **2f** was also photoirradiated with UV light (300-400 nm) of a super high-pressure UV lamp (500W, USIO Inc., Japan) equipped with a U-360 UV transmitting, visible absorbing filter and HA-50 heat absorbing filter to cut off visivle and heat.

Table S5. Effect of additive for first-order rate constants at 20 °C under irradiation

Entry	Wavelength of light	Solvent	Additive	$10^4\ k_{obs}$ (s^{-1})
1	under dark	benzene	none	1.63±0.00
2	visible light	benzene	none	24.6±0.4
3	visible light	benzene	2,6-di(*tert*-butyl)phenol (8.1 mM)	31.3±0.6
4	visible light	benzene	*p*-methoxyphenol (3.0 mM)	27.1±0.5
5	visible light	benzene	^{t}Bu$_2$bpy (3.2 mM)	22.8±0.3
6	visible light	THF	none	19.4±0.3
7	visible light	THF	[PPN][Mn(CO)$_5$] (3.4 mM)	14.2±0.2
8	visible light	acetone	none	10.4±0.1
9	UV light	benzene	none	11.9 ±0.3

The photochemical quantum yield for the reductive elimination process of 2f

The photochemical quantum yield for the reductive elimination process of **2f** was briefly estimated using chemical actinometry. Intensity of the irradiating visible light wiht HA-50 and Y-50 filters to cut off UV light and heat was estimated as 2.91×10^{-9} einsteins s^{-1} by using a potassium ferrioxalate ($\phi = 0.15$ at 546 nm)[8]. Monitoring of the reaction by UV−vis spectrophotometry gave a quantum yield as 0.50 for the photo-induced reductive elimination of **2f**.

DFT Calculation of trimethyl and dimethylphenylplatinum-manganesepentacarbonyl complexes.

DFT calculations of (bpy)Me_2RPt–Mn$(CO)_5$ (R = Me (**1a**), Ph (**1c**)) were performed with the Spartan06 program package (Wavefunction, Inc., Irvine, CA) at the B3LYP level using the LACVP*. The optimized structures represent the equilibrium geometries of the molecules in gas phase. Based on the computed results, reductive elimination of dimenthylphenylplatinum complex giving methyl manganese complex and PtMePh(bpy) is exothermic (ΔE = -11.3 $kJmol^{-1}$), whereas those for trimethylplatinum complex are endothermic (ΔE = 12.2 $kJmol^{-1}$).

Table S6. Computed total energies using DFT optimized at the B3LYP level using the LACVP* basis set for (bpy)Me_2RPt–Mn$(CO)_5$ (R = Me (**1a**), Ph (**1c**)) and methyl transfer products.

Entry	Complex	E/au	E/$kJmol^{-1}$
1	(bpy)Me_3Pt–Mn$(CO)_5$ (**1a**)	-1404.9552461	-3688712.58
2	(bpy)Me_2PhPt–Mn$(CO)_5$ (**1c**)	-1596.6883501	-4192108.20
3	PtMe_2(bpy)	-694.413358	-1823183.55
4	PtMePh(bpy)	-886.155417	-2326602.68
5	MnMe$(CO)_5$	-710.537247	-1865516.85

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