Supporting information for

**Molybdenum-Mediated Vinylidene Rearrangement of Internal Acylalkynes and Sulfonylalkynes**

Takuya Kuwabara, Kousuke Sakajiri, Yousuke Oyama, Shintaro Kodama, and Youichi Ishii
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551 Japan

Table of contents

1. Experimental details ........................ S1–4
2. Molecular structure of 2e (rotamer A) ........................ S5
3. Preliminary molecular structure of 2b (rotamer A) ........................ S6
4. X-ray Crystallographic data for 2d,e, 3 and 4 ........................ S7
5. Details for the 13C-labeling experiments ........................ S8
6. Details for theoretical calculations of 2d ........................ S9
7. 1H, 31P{1H} and 13C{1H} NMR charts for the new compounds ........................ S10–25
8. References ........................ S26
1. Experimental details

General Considerations.

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. Dichloromethane (CH$_2$Cl$_2$) were dried and distilled over P$_4$O$_{10}$, degassed, and stored under argon. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. Silica gel for column chromatography was purchased from Kanto Chemical Co. and used as received. Column chromatography for the purification of 3 was carried out under an argon gas flow. $^{13}$C-enriched phenylacetylene (PhC≡$^{13}$CH) was purchased from Taiyo Nippon Sanso Co. and used as a ca. 25% $^{13}$C-enriched reagent to prepare PhC≡$^{13}$CCOPh by the literature method.$^1$ [(η$^7$-C$_7$H$_7$)MoBr(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane),$^2$ NaBAR$_4^+$·2H$_2$O (Ar$^F$ = 3,5-bis(trifluoromethyl)phenyl),$^3$ PhC≡CCO(p-Tol),$^1$ (p-Ans)C≡CCOPh,$^1$ (1-Naph)C≡CCOPh,$^1$ (cyclo-C$_{3}$H$_3$)C≡CCOPh,$^4$ PhC≡CCOME,$^5$ PhC≡CCHO,$^6$ (p-Ans)C≡CCOO(p-Tol),$^7$ (p-Ans)C≡CSO$_2$Ph,$^7$ and MeC≡CSO$_2$Ph$^8$ were prepared by the literature methods. $^1$H (500 MHz), $^{13}$C($^1$H) (126 MHz), and $^{31}$P($^1$H) (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer at 20 °C unless otherwise stated. Chemical shifts are reported in $\delta$ and referenced to residual $^1$H and $^{13}$C signals of deuterated solvents as internal standards or to the $^{31}$P signal of PPh$_3$ ($\delta$ = 5.65) as an external standard. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. X-ray crystallographic analyses were performed on a Rigaku/MSC VariMax/Saturn CCD diffractometer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by $^1$H NMR spectroscopy. Diffraction data for 2d,e, 3, 4 were collected on a VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71070 Å) at -160 °C. Intensity data were corrected for Lorentz-polarization effects and for empirical absorption (REQAB).$^9$ The structures were solved by a direct method (SIR-2014)$^{10}$ and refined by a full-matrix-least-square method on F$^2$ for all reflections using SHELXL-2014 program.$^{11}$ All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters.

[(η$^7$-C$_7$H$_7$)Mo=C=Ph(CO(p-Tol))(dppe)][BAR$_4^+$] (2b). Complex 2b was synthesized from [(η$^7$-C$_7$H$_7$)MoBr(dppe)] (1) (40.6 mg, 0.061 mmol), PhC≡CCO(p-Tol) (16.4 mg, 0.075 mmol) and NaBAR$_4^+$·2H$_2$O (61.2 mg, 0.066 mmol) and isolated as orange crystals (49.9 mg, 0.030 mmol, 49% yield) by recrystallization from diethyl ether/hexane. For Rotamer A: Selected $^1$H NMR (CDCl$_3$): $\delta$ 6.83 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H, $p$-H of C=CPH), 6.61 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, $m$-H of C=CPH), 5.39 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H, $o$-H of C=CPH), 5.00 (t, $^3$J$_{PH}$ = 2.9 Hz, C=H$_7$ overlapping with C=H$_7$ signal of rotamer B), 2.69 (br, 2H, dppe), 2.38 (s, 3H, CH$_3$), 2.13 (br, dppe, overlapping with CH$_3$ signal of rotamer B). $^{31}$P($^1$H) NMR (CDCl$_3$): $\delta$ 55.0 (s, dppe). Selected $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 367.1 (t, $^2$J$_{CP}$ = 29 Hz, Mo=C=C), 191.9 (t, $^4$J$_{CP}$ = 7 Hz, C=O), 93.9 (s, C=H$_7$), 21.8 (s, CH$_3$). For Rotamer B: Selected $^1$H NMR (CDCl$_3$): $\delta$ 6.72 (d, $^3$J$_{HH}$ = 7.8 Hz, 4H, $m$-H of p-Tol + $o$-H of C=CPH), 6.41 (d, $^3$J$_{HH}$ = 7.8 Hz, 4H, $m$-H of p-Tol + $o$-H of C=CPH), 6.13 (s, 1H, $o$-H of C=CPH), 5.98 (t, $^3$J$_{PH}$ = 2.9 Hz, C=H$_7$), 2.69 (br, 2H, dppe), 2.38 (s, 3H, CH$_3$), 2.13 (br, dppe, overlapping with CH$_3$ signal of rotamer B). $^{31}$P($^1$H) NMR (CDCl$_3$): $\delta$ 55.0 (s, dppe). Selected $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 367.1 (t, $^2$J$_{CP}$ = 29 Hz, Mo=C=C), 191.9 (t, $^4$J$_{CP}$ = 7 Hz, C=O), 93.9 (s, C=H$_7$), 21.8 (s, CH$_3$).

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4H, o-H of p-Tol), 4.98 (t, \(J_{PH} = 3.1\) Hz, C=H\textsubscript{7}, overlapping with C=H\textsubscript{7} signal of rotamer A), 3.45 (br, 2H, dppe), 2.84 (br, 2H, dppe), 2.16 (s, CH\textsubscript{3}, overlapping with dppe signal of rotamer A). \(^{31}\text{P}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 55.2 (s, dppe). Selected \(^{13}\text{C}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 371.0 (Mo=\text{C}=\text{C}), 190.4 (t, \(J_{CP} = 6\) Hz, C=O), 94.0 (s, C=H\textsubscript{7}), 21.5 (s, CH\textsubscript{3}). IR (KBr, cm\textsuperscript{-1}): 1647 (\textnu\textsubscript{C}=O). Anal. Caled for C\textsubscript{81}H\textsubscript{53}BF\textsubscript{24}MoOP\textsubscript{2} (2b): C, 58.29; H, 3.32. Found: C, 57.93; H, 3.17.

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[(\eta^7\text{-C}_7\text{H}_7)\text{Mo} (=\text{C} (=\text{Ans}) (=\text{COPh}) (=\text{dppe}) (=\text{BAR})_{4}] (2c).
\]
Complex 2c was synthesized from 
\([(\eta^7\text{-C}_7\text{H}_7)\text{MoBr}(\text{dppe})] (1) (40.9 mg, 0.062 mmol), (\text{p-Ans})\text{C} (=\text{COPh} (18.0 mg, 0.076 mmol) and NaBAR\textsubscript{4}2H\textsubscript{2}O (61.0 mg, 0.066 mmol) and isolated as orange crystals (34.2 mg, 0.020 mmol, 33% yield) by recrystallization from diethyl ether/hexane. For Rotamer A: Selected \(^1\text{H} NMR (CDCl\textsubscript{3}): \delta 6.12 (d, \(J_{HH} = 8.8\) Hz, 2H, m-H of \text{p-Ans}), 5.15 (d, \(J_{HH} = 8.8\) Hz, 2H, o-H of \text{p-Ans}), 4.97 (C=H\textsubscript{7}, overlapping with C=H\textsubscript{7} signal of rotamer B), 3.53 (s, 3H, OMe), 2.69 (br, 2H, dppe), 2.06 (br, 2H, dppe). \(^{31}\text{P}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 56.7 (s, dppe). Selected \(^{13}\text{C}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 367.4 (M\text{o}=\text{C}=\text{C}), 192.2 (t, \(J_{CP} = 9\) Hz, C=O), 158.0 (s, COMe), 93.0 (s, C\text{C}=\text{H}), 54.1 (s, OCH\textsubscript{3}). For Rotamer B: Selected \(^1\text{H} NMR (CDCl\textsubscript{3}), \delta 6.91 (t, \(J_{HH} = 7.0\) Hz, 2H, m-H of \text{C}(=\text{O})\text{Ph}), 6.84 (d, \(J_{HH} = 8.5\) Hz, 2H, m-H of \text{p-Ans}), 6.61 (d, \(J_{HH} = 8.5\) Hz, 2H, o-H of \text{p-Ans}), 6.43 (d, \(J_{HH} = 7.0\) Hz, 2H, o-H of \text{C}(=\text{O})\text{Ph}), 3.76 (s, 3H, OMe), 3.45 (br, 2H, dppe), 2.84 (br, 2H, dppe). \(^{31}\text{P}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 55.9 (s, dppe). Selected \(^{13}\text{C}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 370.9 (M\text{o}=\text{C}=\text{C}), 190.2 (s, C=O), 158.4 (s, COMe), 93.0 (s, C\text{C}=\text{H}), 54.3 (s, OCH\textsubscript{3}). IR (KBr, cm\textsuperscript{-1}): 1648 (\textnu\textsubscript{C}=O). Anal. Caled for C\textsubscript{81}H\textsubscript{53}BF\textsubscript{24}MoOP\textsubscript{2} (2c): C, 57.74; H, 3.29. Found: C, 57.55; H, 2.90.

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[(\eta^7\text{-C}_7\text{H}_7)\text{Mo} (=\text{C} (=\text{cyclo-C}_3\text{H}_5) (=\text{COPh}) (=\text{dppe}) (=\text{BAR})_{4}] (2d).
\]
Complex 2d was synthesized from 
\([(\eta^7\text{-C}_7\text{H}_7)\text{MoBr}(\text{dppe})] (1) (121 mg, 0.182 mmol), (\text{cyclo-C}_3\text{H}_5)\text{C} (=\text{COPh} (62.8 mg, 0.369 mmol) and NaBAR\textsubscript{4}2H\textsubscript{2}O (182 mg, 0.198 mmol) and isolated as orange crystals (107 mg, 0.066 mmol, 37% yield) by recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/hexane. For Rotamer A: Selected \(^1\text{H} NMR (CDCl\textsubscript{3}): 4.73 (t, \(J_{HP} = 3.5\) Hz, 7H, C=H\textsubscript{7}), 2.84–2.60 (m, 2H, dppe), −0.06 (m, 1H, CH\textsubscript{2}(CH\textsubscript{2})), −0.12 (m, 2H, CH\textsubscript{2}(CH\textsubscript{2})), −0.46 (m, 2H, CH\textsubscript{2}(CH\textsubscript{2})). \(^{31}\text{P}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 51.6 (s, dppe). Selected \(^{13}\text{C}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 370.6 (t, \(J_{CP} = 30\) Hz, M\text{o}=\text{C}=\text{C}), 191.2 (t, \(J_{CP} = 7\) Hz, C=O), 92.9 (s, C\text{C}=\text{H}), 11.4 (t, \(J_{CP} = 8\) Hz, cyclo-C\textsubscript{3}H\textsubscript{5}), 5.8 (s, cyclo-C\textsubscript{3}H\textsubscript{5}). For Rotamer B: Selected \(^1\text{H} NMR (CDCl\textsubscript{3}): 7.29 (t, \(J_{HH} = 7.5\) Hz, 1H, p-H of \text{C}(=\text{O})\text{Ph}), 7.13 (t, \(J_{HH} = 7.5\) Hz, 2H, m-H of \text{C}(=\text{O})\text{Ph}), 6.75 (d, \(J_{HH} = 7.5\) Hz, 2H, o-H of \text{C}(=\text{O})\text{Ph}), 5.19 (t, \(J_{HP} = 3.0\) Hz, 7H, C=H\textsubscript{7}). \(^{31}\text{P}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 54.3 (s, dppe). Selected \(^{13}\text{C}\{^1\text{H}\} NMR (CDCl\textsubscript{3}): \delta 93.3 (s, C=\text{H}). No \(^{13}\text{C}\{^1\text{H}\} NMR signal attributable to the vinylidene \alpha\text{-carbon and the carbonyl carbon could be observed. IR (KBr, cm}\textsuperscript{-1}): 1650 (\textnu\textsubscript{C}=O). Anal. Caled for C\textsubscript{71}H\textsubscript{54}BF\textsubscript{24}MoOP\textsubscript{2} (2d): C, 57.13; H, 3.30. Found: C, 57.43; H, 3.24.

\[
[(\eta^7\text{-C}_7\text{H}_7)\text{Mo} (=\text{C} (=\text{COMe}) (=\text{dppe}) (=\text{BAR})_{4}] (2e).
\]
Complex 2e was synthesized from 
\([(\eta^7\text{-C}_7\text{H}_7)\text{MoBr}(\text{dppe})] (1) (40.8 mg, 0.061 mmol), \text{PhC}=\text{C} \text{COMe} (10.5 mg, 0.073 mmol) and NaBAR\textsubscript{4}2H\textsubscript{2}O (61.0 mg, 0.066 mmol) and isolated as orange crystals (33.8 mg, 0.021 mmol, 35%
yield) by recrystallization from diethyl ether/hexane. For **Rotamer A**: Selected $^1$H NMR (CDCl$_3$): δ 6.87 (t, $^3$$J_{HH} = 7.8$ Hz, 1H, $p$-H of C=CPh), 6.60 (t, $^3$$J_{HH} = 7.8$ Hz, 2H, $m$-H of C=CPh), 5.30 (t, $^3$$J_{HP} = 3.3$ Hz, 7H, C=H$_7$), 4.97 (dd, $^4$$J_{HH} = 7.8$ Hz, $^4$$J_{HH} = 1.5$ Hz, 2H, $o$-H of C=CPh), 2.59 (br, 2H, dppe), 1.68 (br, 2H, dppe), 1.66 (s, 3H, COMe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 58.5 (s, dppe). Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 370.2 (t, $^2$$J_{CP} = 29$ Hz, Mo=C=C), 202.2 (t, $^2$$J_{CP} = 6$ Hz, C=O), 94.6 (s, C=H$_7$), 30.7 (s, CH$_3$). For **Rotamer B**: Selected $^1$H NMR (CDCl$_3$): δ 6.84 (dd, $^3$$J_{HH} = 8.1$ Hz, $^4$$J_{HH} = 1.2$ Hz, 2H, $o$-H of C=CPh), 4.88 (t, $^3$$J_{HP} = 3.3$ Hz, 7H, C=H$_7$), 3.40 (br, 2H, dppe), 2.73 (br, 2H, dppe), 1.02 (s, 3H, COMe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 54.3 (s, dppe).Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 368.5 (t, $^2$$J_{CP} = 29$ Hz, Mo=C=C), 195.2 (t, $^2$$J_{CP} = 6$ Hz, C=O), 93.8 (s, C=H$_7$), 28.4 (s, CH$_3$).

IR (KBr, cm$^{-1}$): 1665 (vC=O). Anal. Caled for C$_7$H$_5$BF$_4$MoO$_2$: C, 56.55; H, 3.23. Found: C, 56.56; H, 2.93.

$$[(\eta^2$-C$_{2}$H$_{2})$Mo($\equiv$C=CPh(CHO))(dppe)](BF$_4$) (2f). Complex 2f was synthesized from $$[(\eta^2$-C$_{2}$H$_{2})$MoBr(dppe)] (I) (39.9 mg, 0.060 mmol), PhC=CCCHO (9.7 mg, 0.075 mmol) and NaBF$_4$·2H$_2$O (60.8 mg, 0.066 mmol) and isolated as orange crystals (21.7 mg, 0.014 mmol, 23% yield) by recrystallization from diethyl ether/hexane. For **Rotamer A**: Selected $^1$H NMR (CDCl$_3$, 233 K): δ 9.44 (s, 1H, CHO), 6.87 (t, $^3$$J_{HH} = 7.5$ Hz, 1H, $p$-H of C=CPh), 6.64 (t, $^3$$J_{HH} = 7.5$ Hz, 2H, $m$-H of C=CPh), 5.37 (s, 7H, C=H$_7$), 4.97 (d, $^3$$J_{HH} = 7.5$ Hz, 1H, $o$-H of C=CPh), 2.70 (br, 2H, dppe), 1.91 (br, 2H, dppe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 57.6 (s, dppe). Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 94.8 (s, C=H$_7$). No $^{13}$C$^1$$^1$H NMR signal attributable to the vinylidene $\alpha$-carbon and the formyl group could be observed. For **Rotamer B**: Selected $^1$H NMR (CDCl$_3$, 233 K): δ 7.93 (s, 1H, CHO), 6.83 (d, $^3$$J_{HH} = 7.7$ Hz, 2H, $o$-H of C=CPh), 5.12 (s, 7H, C=H$_7$), 3.09 (br, 2H, dppe), 2.92 (br, 2H, dppe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 54.2 (s, dppe). Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 373.6 (t, $^2$$J_{CP} = 29$ Hz, Mo=C=C), 186.8 (s, C=O), 94.5 (s, C=H$_7$). IR (KBr, cm$^{-1}$): 1672 (vC=O). Anal. Caled for C$_7$H$_5$BF$_4$MoO$_2$: C, 56.29; H, 3.13. Found: C, 56.61; H, 2.90.

$$[(\eta^2$-C$_{2}$H$_{2})$Mo($\equiv$C-Ans)(CHO))(dppe)](BF$_4$) (2g). Complex 2g was synthesized from $$[(\eta^2$-C$_{2}$H$_{2})$MoBr(dppe)] (I) (39.8 mg, 0.060 mmol), (p-Ans)C=CCCHO (11.7 mg, 0.072 mmol) and NaBF$_4$·2H$_2$O (60.9 mg, 0.066 mmol) and isolated as orange crystals (31.2 mg, 0.019 mmol, 32% yield) by recrystallization from diethyl ether/hexane. For **Rotamer A**: Selected $^1$H NMR (CDCl$_3$, 233 K): δ 9.41 (s, 1H, CHO), 6.14 (d, $^3$$J_{HH} = 8.5$ Hz, 2H, $m$-H of p-Ans), 5.34 (s, 7H, C=H$_7$), 4.83 (d, $^3$$J_{HH} = 8.5$ Hz, $o$-H of p-Ans), 3.55 (s, 3H, OMe), 2.68 (br, 2H, dppe), 1.92 (br, 2H, dppe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 57.5 (s, dppe). Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 194.2 (s, C=O), 159.2 (s, COMe), 94.7 (s, C=H$_7$), 55.1 (s, OCH$_3$). No $^{13}$C$^1$$^1$H NMR signal attributable to the vinylidene $\alpha$-carbon could be observed. For **Rotamer B**: Selected $^1$H NMR (CDCl$_3$, 233 K): δ 7.89 (s, 1H, CHO), 6.92 (d, $^3$$J_{HH} = 8.5$ Hz, 2H, $m$-H of p-Ans), 6.72 (d, $^3$$J_{HH} = 8.5$ Hz, 2H, $o$-H of p-Ans), 5.09 (s, 7H, C=H$_7$), 3.79 (s, 3H, OMe), 3.01 (br, 2H, dppe), 2.88 (br, 2H, dppe). $^{31}$P$^1$$^1$H NMR (CDCl$_3$): δ 54.1 (s, dppe). Selected $^{13}$C$^1$$^1$H NMR (CDCl$_3$): δ 374.7 (t, $^2$$J_{CP} = 31$ Hz, Mo=C=C), 186.9 (s, C=O), S3
159.8 (s, COMe), 94.4 (s, C\textsubscript{7}H\textsubscript{7}), 55.4 (s, OCH\textsubscript{3}). IR (KBr, cm\textsuperscript{-1}): 1664 (v=C=O). Anal. Calcd for C\textsubscript{75}H\textsubscript{51}BF\textsubscript{24}MoO\textsubscript{2}P\textsubscript{2} (2g): C, 55.99; H, 3.20. Found: C, 55.87; H, 3.14.

\[ ([\eta^7\text{-C}_{7}H_{7}]Mo[=C=C(1-Naph)(COPh)](dppe)]\text{[BAr}^{\text{F}}\text{4}] \text{(2h).} \]

Complex 2h was synthesized from \([([\eta^7\text{-C}_{7}H_{7}]MoBr(dppe)] \text{(1) (40.4 mg, 0.061 mmol), (1-Naph)C≡CCOPh (19.1 mg, 0.075 mmol) and NaBAr^{F}4·2H\text{2O (61.5 mg, 0.067 mmol) and isolated as orange crystals (42.5 mg, 0.025 mmol, 41\% yield) by recrystallization from diethyl ether/hexane. For Rotamer A: selected }^{1}\text{H NMR (CDCl}_{3}\text{): }\delta \text{ 5.29 (s, 7H, C}_{7}\text{H}_{7}).} \]

\[ ^{31}\text{P}\{^{1}\text{H}\} \text{NMR (CDCl}_{3}\text{): }\delta \text{ 56.3 (s, dppe).} \]

\[ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (CDCl}_{3}\text{): }\delta \text{ 94.9 (s, C}_{7}\text{H}_{7}). \]

No \[ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR signal attributable to the vinylidene }\alpha\text{-carbon and the carbonyl carbon could be observed. For Rotamer B: Selected }^{1}\text{H NMR (CDCl}_{3}\text{): }\delta \text{ 7.05 (t, 1H, p-H of C(=O)Ph), 6.81 (t, }^{3}J_{HH} \text{= 7.5 Hz, 2H, m-H of C(=O)Ph), 6.50 (d, }^{3}J_{HH} \text{= 7.5 Hz, 2H, o-H of C(=O)Ph), 4.80 (s, 7H, C}_{7}\text{H}_{7}), 3.52 (br, 2H, dppe), 2.65 (br, 2H, dppe).} \]

\[ ^{31}\text{P}\{^{1}\text{H}\} \text{NMR (CDCl}_{3}\text{): }\delta \text{ 54.4 (s, dppe).} \]

Selected \[ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (CDCl}_{3}\text{): }\delta \text{ 370.9 (t, }^{2}J_{CP} \text{= 28 Hz, Mo=C=C), 191.9 (t, }^{4}J_{CP} \text{= 6 Hz, C=O), 94.1 (s, C}_{7}\text{H}_{7}). \]

IR (KBr, cm\textsuperscript{-1}): 1647 (v=C=O). Anal. Calcd for C\textsubscript{84}H\textsubscript{55}BF\textsubscript{24}MoOP\textsubscript{2} (2h): In spite of repeated elemental analyses, satisfactory analytical data could not be obtained for 2h. However, purity of the isolated sample of 2h was confirmed to be high on the basis of the \[ ^{1}\text{H} \text{and } ^{31}\text{P}\{^{1}\text{H}\} \text{NMR spectra.} \]
2. Molecular structure of 2e (rotamer A)

Figure S1. Molecular structures of the cationic part of 2e from two different angles with thermal ellipsoid plot at 50% probability. All hydrogen atoms and a 'Butyl methyl ether molecule are omitted for clarity. Selected bond lengths (Å): Mo–C(1), 1.939(6); C(1)–C(2), 1.311(8). The angle made by the C7H7 and C1–C2–C3–C4 planes is 88.7°, while the C*–Mo–C1 and C(1)–C(2)–C(3)–C(4) planes form a dihedral angle of 3.8°, where C* is the center of the C7H7 ring.
3. Preliminary molecular structure of 2b (rotamer A)

Figure S2. Preliminary molecular structure of the cationic part of 2b with thermal ellipsoid plot at 50% probability. The angle made by the C7H7 and C1−C2−C3−C4 planes is 78.7°, while the C*−Mo−C1 and C(1)−C(2)−C(3)−C(4) planes form a dihedral angle of 11.6°, where C* is the center of the C7H7 ring.
4. X-ray crystallographic data for 2d, e, 3 and 4.

Table S1. X-ray crystallographic data for 2d, e, 3 and 4.

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<td>1.134/-1.02</td>
<td>1.03/-1.15</td>
<td>1.61/-1.41</td>
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\textsuperscript{a} R\textsubscript{I} = \sum|F\textsubscript{o}|-|F\textsubscript{c}|/\sum|F\textsubscript{o}|.  
\textsuperscript{b} wR\textsubscript{2} = \sqrt{\sum(w(F\textsubscript{o}^2 - F\textsubscript{c}^2)^2)/\sum w(F\textsubscript{o}^2)^2} \times 100, \text{ w = 1} /[\sigma^2 F\textsubscript{o}^2 + (aP)^2 + bP] \text{ (a and b are constants suggested by the refinement program; P = [max(F\textsubscript{o}^2,0) + 2F\textsubscript{c}^2]/3).}  
\textsuperscript{c} GOF = \sqrt{\sum w(F\textsubscript{o}^2 - F\textsubscript{c}^2)^2(N\textsubscript{obs} - N\textsubscript{params})}\times 100.
5. Details for the $^{13}$C-labeling experiments

$^{13}$C-labeling experiment

Complex $2a-^{13}C_\alpha$ was synthesized from $[(\eta^7-C_7H_7)MoBr(dppe)]$ (1) (40.8 mg, 0.061 mmol), PhC$^{=^{13}}$CCOPh (13.1 mg, 0.064 mmol) and NaBAR$^f\cdot 2$H$\_2$O (67.1 mg, 0.073 mmol), and obtained as orange crystals (28.5 mg, 0.017 mmol, 28% yield) by recrystallization from diethyl ether/hexane.

$^{13}$C NMR analysis

The generation ratio of $2a-^{13}C_\alpha$ and $2a-^{13}C_\beta$ was estimated from the $^{13}$C{^1}H NMR. The relative integration ratio of the $C_\alpha$ signals in the $^{13}$C-labeling and non-labeling experiments based on the $C_\beta$ signals is:

$$^{13}C_\alpha$ in $^{13}$C-labeling experiment:$^{13}C_\alpha$ in non-labeling experiment = 0.91:0.03

Taking into account that the alkyne reagent is 25% $^{13}$C-enriched, and the natural abundance of $^{13}$C is 1.1%, the ratio of $C_\alpha$ signals between the two experiments can be calculated as:

$$^{13}C_\alpha$ in $^{13}$C-labeling experiment:$^{13}C_\alpha$ in non-labeling experiment = $0.25t + 0.011(1 - t)$:0.011,

where $t$ = the migration ratio of the COPh group.

Thus $t$ is calculated to be 1.03 by solving the following equation:

$$\{0.25t + 0.011(1 - t)\} \times 0.03 = 0.011 \times 0.91$$

This calculation revealed that the migration ratio of the COPh group is essentially 100%.

![Figure S3. Comparison of $^{13}$C{^1}H NMR charts of $^{13}$C-labeling (upper) and non-labeling (lower) experiments.](image_url)
6. Details for the theoretical calculations of 2d

Theoretical calculations were performed using the gaussian 09 program. Single point calculations (without optimization) were carried out based on the structure revealed by X-ray diffraction study with hybrid density functional theory at B3PW91 level using the Lanl2dz basis set for Mo and 6-31G(d,p) for the others.

Figure S4. HOMO−2 of 2d with iso value of 0.04 au. Mo, blue; P, orange; O, red; C, gray.
7. $^1\text{H}$, $^{31}\text{P}^1\text{H}$ and $^{13}\text{C}^1\text{H}$ NMR charts for the new compounds

Figure S5. $^1\text{H}$ NMR spectrum of 2a recorded in CDCl$_3$.

Figure S6. $^{31}\text{P}^1\text{H}$ NMR spectrum of 2a recorded in CDCl$_3$. 
Figure S7. $^{13}$C{$_1^1$H} NMR spectrum of 2a recorded in CDCl$_3$.

Figure S8. $^1$H NMR spectrum of 2b recorded in CDCl$_3$. 
Figure S9. $^{31}$P{${}^1$H} NMR spectrum of 2b recorded in CDCl$_3$.

Figure S10. $^{13}$C{${}^1$H} NMR spectrum of 2b recorded in CDCl$_3$. 
Figure S11. $^1$H NMR spectrum of 2c recorded in CDCl$_3$.

Figure S12. $^{31}$P{$^1$H} NMR spectrum of 2c recorded in CDCl$_3$. 
Figure S13. $^{13}$C{$^{1}$H} NMR spectra of 2c recorded in CDCl3.

Figure S14. $^1$H NMR spectrum of 2d recorded in CDCl3.
Figure S15. $^{31}$P{$^1$H} NMR spectrum of 2d recorded in CDCl$_3$.

Figure S16. $^{13}$C{$^1$H} NMR spectrum of 2d recorded in CDCl$_3$. 
Figure S17. $^1$H NMR spectrum of 2e recorded in CDCl$_3$.

Figure S18. $^{31}$P$\{^1$H$\}$ NMR spectrum of 2e recorded in CDCl$_3$. 
Figure S19. $^{13}$C\{$^1$H\} NMR spectrum of $2e$ recorded in CDCl$_3$.

Figure S20. $^1$H NMR spectrum of $2f$ recorded in CDCl$_3$ at $-40 \, ^\circ C$. 
Figure S21. $^{31}$P{$^1$H} NMR spectrum of 2f recorded in CDCl$_3$.

Figure S22. $^{13}$C{$^1$H} NMR spectrum of 2f recorded in CDCl$_3$. 
Figure S23. $^1$H NMR spectrum of 2g recorded in CDCl$_3$ at −40 °C.

Figure S24. $^{31}$P{$^1$H} NMR spectrum of 2g recorded in CDCl$_3$. 
Figure S25. $^{13}$C{\textsuperscript{1}H} NMR spectrum of 2g recorded in CDCl$_3$.

Figure S26. $^1$H NMR spectrum of 2h recorded in CDCl$_3$. 
Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2h recorded in CDCl$_3$.

Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2h recorded in CDCl$_3$. 
Figure S29. $^1$H NMR spectrum of 3 recorded in CDCl$_3$.

Figure S30. $^{31}$P{$^1$H} NMR spectrum of 3 recorded in CDCl$_3$. 
Figure S31. $^{13}$C{\textsuperscript{1}H} NMR spectrum of 3 recorded in CDCl$_3$.

Figure S32. $^1$H NMR spectrum of 4 recorded in CD$_2$Cl$_2$. 
Figure S33. $^{13}$C{$_1^1$H} NMR spectrum of 4 recorded in CD$_2$Cl$_2$.

Figure S34. $^1$H NMR spectrum of 5 recorded in CD$_2$Cl$_2$. 
Figure S35. $^{13}$C{$^1$H} NMR spectrum of 5 recorded in CD$_2$Cl$_2$. 
References


(12) Although this signal should be observed as a triplet. J value could not be determined because of the low intensity of the singal.


