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Cationic molybdenum complexes with P-coordinated (diphenylphosphino)alkynes

Elmostafa Louattani, Joan Suades *

Departament de Química, Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

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Abstract

New cationic P-coordinated (diphenylphosphino)alkyne complexes with molybdenum $[(Mp)Ph_2PC{\equiv}CR][BF_4]$ {R = H, Me, ^{t}Bu, Ph, Tol; Mp = $(C_5H_5)Mo(CO)_3$} have been prepared from reaction between a (diphenylphosphino)alkyne $Ph_2PC{\equiv}CR$ and the dinuclear complex $[(C_5H_5)Mo(CO)_3]_2$, with Ag(I) as oxidant. The bis(diphenyphosphosphino)acetylene $Ph_2PC{\equiv}CPPh_2$ led to the following homo- and heteronuclear metal complexes by the same method: $[(Mp)Ph_2PC{\equiv}CPPh_2][BF_4]$, $[(Mp)Ph_2PC{\equiv}CPPh_2(Mp)][BF_4]_2$ and $[(Mp)Ph_2PC{\equiv}CPPh_2(Fp)][BF_4]_2$ {Fp = $(C_5H_5)Fe(CO)_2$}. The reaction of the P-coordinated molybdenum complexes $[(Mp)Ph_2PC{\equiv}CR][BF_4]$ with dicobalt octacarbonyl at room temperature afforded the cationic heterometallic complexes $[(Mp)Ph_2PC_2R\{Co_2(CO)_6\}][BF_4]$. All complexes were characterised by microanalysis and IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy.

Keywords: Phosphinoalkyne; Carbonyl; Cyclopentadienyl; Molybdenum; Cobalt; Iron

1. Introduction

The acetylenic phosphines $Ph_2PC{\equiv}CR$ have been extensively studied as ligands in transition metal chemistry. The phosphine and the alkyne functions are usually involved in reactions with polynuclear metal complexes [1], but P-coordinated transition metal complexes with the uncoordinated alkyne have also been reported [2]. In previous papers, we have described the synthesis of anionic $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CR)]$ [3], cationic $[(Fp)Ph_2PC{\equiv}CR][BF_4]$ {Fp = $(C_5H_5)Fe(CO)_2$} [4] and zwitterionic P-coordinated iron complexes [5]. The study of the uncoordinated alkyne in the cationic complexes $[(Fp)Ph_2PC{\equiv}CR][BF_4]$ indicates that the cationic charge located on the phosphorus atom induces a significant CC triple bond polarization in the alkyne function (Scheme 1) [4].

Here we describe the synthesis of a new family of cationic molybdenum complexes with diphenylphosphinoalkynes $[(Mp)Ph_2PC{\equiv}CR]^+$ {Mp = $(C_5H_5)Mo(CO)_3$}. The isolobal relation between the fragments {Mp} and {Fp} suggests the viability of these molybdenum compounds. We aim to compare alkyne polarization in the new molybdenum complexes with previous results on the isolobal iron fragment (Scheme 1). If similar results were obtained, they would provide additional evidence of the isolobal relationship between these iron and molybdenum fragments.

Moreover, the molybdenum complexes $[(Mp)Ph_2PC{\equiv}CR]^+$ may be used as starting materials for the synthesis of mixed cobalt–molybdenum and iron–molybdenum complexes. Indeed, on the basis of the reported synthesis of iron–cobalt complexes $[(Fp)Ph_2PC_2R\{Co_2(CO)_6\}]^+$ [6], the preparation of cobalt–molybdenum compounds seems feasible via the reaction between the uncoordinated alkyne and dicobalt octacarbonyl. Similarly, the synthesis of the iron–molybdenum complex $[(Fp)Ph_2PC{\equiv}CPPh_2(Mp)]^{2+}$ seems viable starting from the iron complex $[(Fp)Ph_2PC{\equiv}CPPh_2]^+$ [5].

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* Corresponding author. Fax: + 34-93-5813101.

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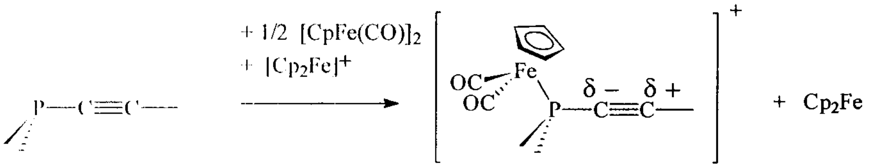
2. Results and discussion

2.1. $[(Mp)Ph_2PC{\equiv}CR][BF_4]$ (1–5)

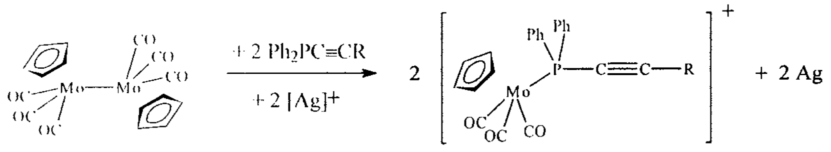
A series of molybdenum cationic P-coordinated (diphenylphosphino)alkyne complexes $[(Mp)Ph_2PC{\equiv}CR]^+$ {R = H (**1**), CH_3 (**2**), ^{t}Bu (**3**), Ph (**4**), Tol (**5**)} were synthesised by oxidation of $[(C_5H_5)Mo(CO)_3]_2$ with $AgBF_4$ in the presence of (diphenylphosphino)alkyne (Scheme 2).

The products were isolated as yellow micro-crystalline solids and characterised by the usual analytical and spectroscopic techniques. The IR spectra of complexes **1**–**5** showed a set of three bands in the 2100–1950 cm^{-1} region, assigned to the terminal ν(CO) bands of the fragment $\{CpMo(CO)_3\}$. Similar values have been reported for the cationic complexes $[(Mp)PR_3]^+$ [7]. This result is consistent with the ^{1}H- and ^{13}C-NMR spectra: the signals corresponding to an η^5-cyclopentadienyl ligand are observed in the ^{1}H- and ^{13}C-NMR spectra, whereas the characteristic bands of the three CO ligands bonded to molybdenum are recognised in the ^{13}C-NMR spectra at 225–227 ppm [8,9]. Indeed, the ^{31}P-NMR spectra of **1**–**6** show signals at 21–24 ppm, which corroborates the P-coordination of the (diphenylphospino)alkyne to the molybdenum atom [10]. Finally, a weak IR band near 2200 cm^{-1} assigned to ν(C≡C) of the free triple bond [11] together with the ^{13}C-NMR signals of the acetylenic carbon atoms are consistent with the presence of an uncoordinated alkyne. All these data are compatible with the structure proposed for complexes **1**–**5** in Scheme 2.

The chemical shift difference $(\delta C_2 - \delta C_1)$ between the acetylenic carbon atoms for different compounds has been related to a polarization of the triple bond [4,12]. Analogously, the sum $(\delta C_2 + \delta C_1)$ has been associated with the charge changes [4,12]. Hence, Table 1 shows these values for iron and molybdenum P-coor-



Scheme 1.

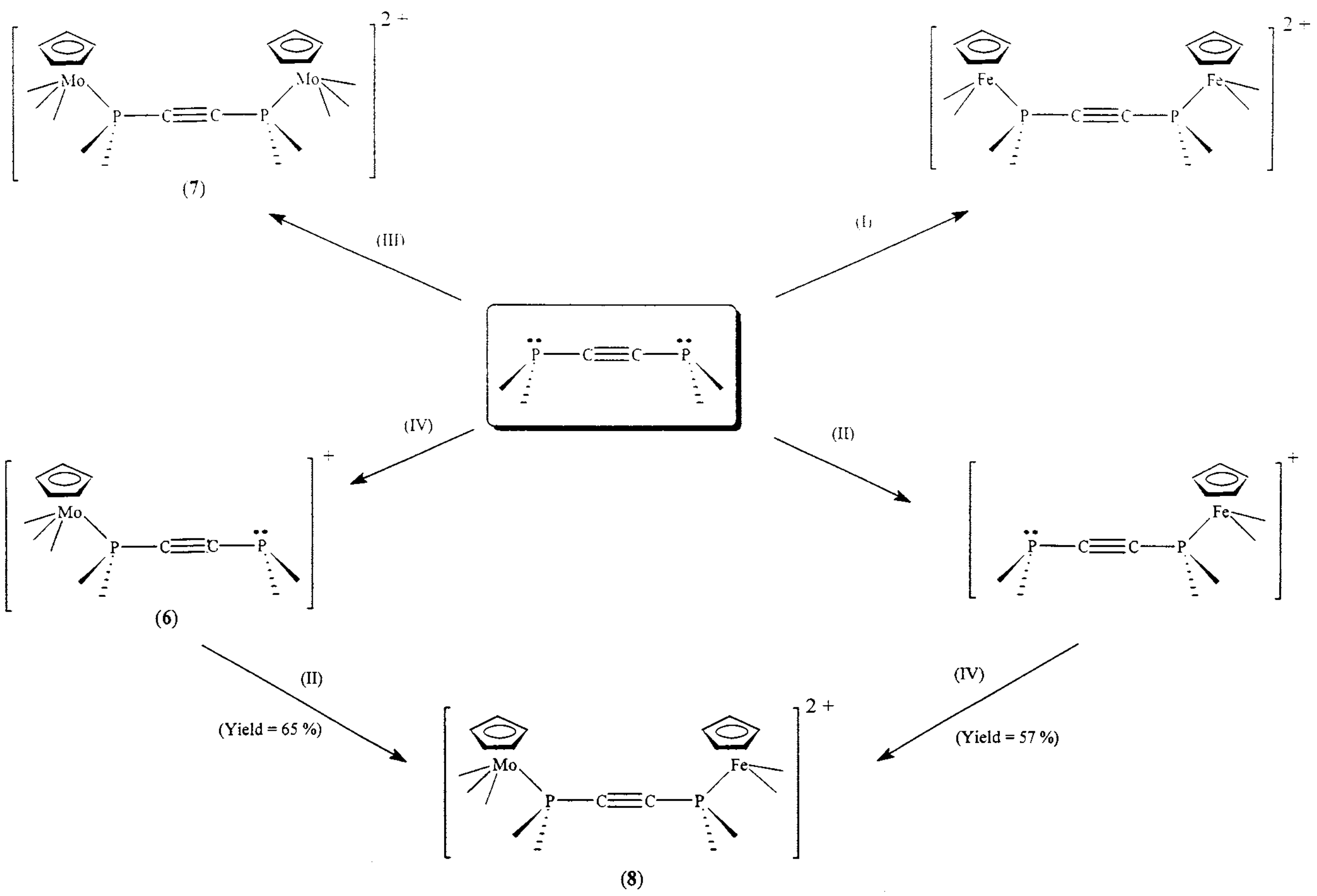


R = H (**1**), CH_3(**2**), tBu(**3**), Ph(**4**), Tol(**5**)

Scheme 2.

Table 1
^{13}C Chemical shifts (δ, ppm) for the acetylenic carbons in cationic complexes $[(X)Ph_2PC{\equiv}CR]^+$ and free phosphinoalkynes $Ph_2PC{\equiv}CR$

R	X	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^1)+\delta(C^2)$	$\delta(C^2)-\delta(C^1)$
H		92.0	98.8	190.8	6.8
H	$CpFe(CO)_2$	76.1	107.0	183.1	30.9
H	$CpMo(CO)_3$	78.5	109.1	187.6	30.6
Me		75.4	107.2	182.6	31.8
Me	$CpFe(CO)_2$	70.9	117.9	188.8	47.0
Me	$CpMo(CO)_3$	74.0	117.3	191.3	43.3
^{t}Bu		75.2	119.5	194.7	44.3
^{t}Bu	$CpFe(CO)_2$	70.9	127.9	198.8	57.0
^{t}Bu	$CpMo(CO)_3$	71.2	128.2	199.4	57.0
Ph		86.5	109.4	195.9	22.9
Ph	$CpFe(CO)_2$	80.3	115.7	196.0	35.4
Ph	$CpMo(CO)_3$	80.6	116.1	196.7	35.5
Tol		85.3	108.9	194.2	23.6
Tol	$CpFe(CO)_2$	80.0	116.5	196.5	36.5
Tol	$CpMo(CO)_3$	79.8	116.7	196.5	36.9



(I) = $[CpFe(CO)_2]_2 + 2\ [FeCp_2]^+$; (II) = $1/2\ [CpFe(CO)_2]_2 + [FeCp_2]^+$; (III) = $[CpMo(CO)_3]_2 + 2\ Ag^+$; (IV) = $1/2\ [CpMo(CO)_3]_2 + Ag^+$

Scheme 3.

dinated phoshinoalkyne complexes. As mentioned above, the comparison between the alkyne polarisation of these two families of complexes may provide information about the electronic behaviour of the isolobal fragments {Mp} and {Fp}. The results obtained for the molybdenum complexes (Table 1) show similar trends to those previously observed with the iron complexes, which can be summarized as follows: (1) there is a small influence of P-coordination on the alkyne charge ($\delta C_2 + \delta C_1$); (2) there is an important effect on the polarization of the C≡C triple bond. Finally, the most remarkable feature in Table 1 is the strong similarity between the values shown by the iron and molybdenum complexes prepared with the same (diphenylphosphino)alkyne. This may be attributable to a similar C≡C polarization in the homologous iron and molybdenum complexes, which denotes a similar electronic influence of the iron and molybdenum fragments on the alkyne function.

*2.2. [(Mp)Ph$_2$PC≡CPPh$_2$][BF$_4$] (**6**) and [(Mp)Ph$_2$PC≡CPPh$_2$(Mp)][BF$_4$]$_2$ (7)*

As shown in Scheme 3, complexes **6** and **7** were prepared by oxidation of the dinuclear complex $[(C_5H_5)Mo(CO)_3]_2$ with $AgBF_4$ in the presence of the diphosphine. By using the appropriate ratio of reagents, complexes **6** and **7** were selectively isolated and characterised by the usual spectroscopic and analytical methods. The different symmetry in **6** and **7** is revealed by their IR and ^{31}P-NMR spectra. Thus, the IR spectrum of **6** shows a band at 2122 cm^{-1} assigned to ν(C≡C), which is absent in **7**; this is consistent with the structures shown in Scheme 3. The ^{31}P-NMR spectrum of **7** shows only one signal at 25.3 ppm assigned to the phosphorus atom coordinated to molybdenum. In contrast, the spectrum of **6** exhibits two signals: one peak at 23.4 ppm, assigned to the phosphorus atom bonded to molybdenum, and another at −20.2 ppm, which is characteristic of an uncoordinated phosphorus atom.

Consequently, the simple synthetic method previously used for the synthesis of the diphenylphosphine iron complexes $[(Fp)Ph_2PC{\equiv}CPPh_2][BF_4]$ and $[(Fp)Ph_2PC{\equiv}CPPh_2(Fp)][BF_4]_2$ [5] may be extended to the synthesis of the homologous molybdenum complexes (Scheme 3).

2.3. $[(Mp)Ph_2PC{\equiv}CPPh_2(Fp)][BF_4]_2$ (**8**)

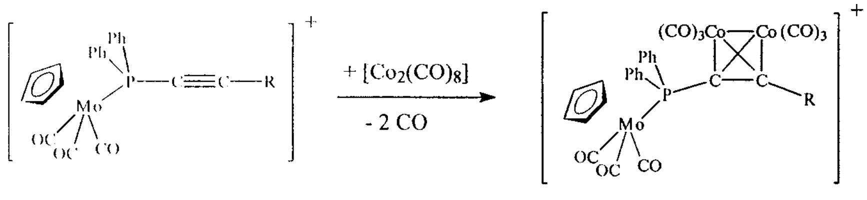
The successful synthesis of mono- and bimetallic iron and molybdenum complexes with $Ph_2PC{\equiv}CPPh_2$ induced us to attempt the preparation of a heterometallic iron–molybdenum complex. As shown in Scheme 3, two synthetic pathways are possible, depending on the starting material: $[(Mp)Ph_2PC{\equiv}CPPh_2][BF_4]$ or $[(Fp)Ph_2PC{\equiv}CPPh_2][BF_4]$. Both methods were performed and the resulting compounds were isolated as yellow microcrystalline solids with comparable yields. Analytical and spectroscopic methods showed that complexes obtained by the two pathways are identical, and their formulations agree with that of the title complex **8**. Thus, the IR spectrum shows a weak band at 2122 cm^{-1} which, in agreement with the proposed heterometallic structure (Scheme 3), is characteristic of an asymmetric arrangement around the C≡C bond. Furthermore, the $\nu(CO)$ region displays a set of bands that are practically superpositions of the characteristic bands of the cationic $\{CpMo(CO)_3\}$ [7] and $\{CpFe(CO)_2\}$ [4] fragments. The asymmetric coordination of $Ph_2PC{\equiv}CPPh_2$ to the two different metallic fragments is corroborated by the ^{31}P-NMR spectrum, which shows two bands at 24.7 and 46.7 ppm: these are, respectively, assigned to the phosphorus atoms bonded to the molybdenum and to the iron fragment [13]. The ^1H- and ^{13}C-NMR spectrum shows the signals of the two different cyclopentadienyl groups bonded to iron and molybdenum atoms, and different carbonyl groups are also observed in the ^{13}C-NMR spectrum.

Finally, the overall synthetic results obtained with bis(diphenylphosphino)acetylene (Scheme 3) confirm its ability to form mono- or bimetallic cationic metal complexes with iron or molybdenum fragments. Since P-coordinated complexes of this ligand with different metals have been reported [14], the simple synthesis displayed in Scheme 3 can be used to prepare new heterometallic complexes.

2.4. $[(Mp)Ph_2PC_2R\{Co_2(CO)_6\}][BF_4]$ (**9–11**) $\{R = CH_3$ (**9**), Ph (**10**), Tol (**11**)$\}$

The reaction between the cationic complexes $[(Mp)Ph_2PC{\equiv}CR]^+$ and $[Co_2(CO)_8]$ at room temperature in dichloromethane afforded the complexes **9–11** (Scheme 4), which were isolated as brown microcrystalline solids and characterised by the usual analytical and spectroscopic techniques. The IR spectrum of **9–11** indicates alkyne coordination since it shows a set of bands at 2100–2000 cm^{-1} with marked similarity to the $\nu(CO)$ absorption of the $Co_2(CO)_6$ fragment [6,15], overlapping the $\nu(CO)$ bands of the $[CpMo(CO)_3]^+$ fragment [7]. The absence of the $\nu(C{\equiv}C)$ band of the uncoordinated alkyne also suggests the coordination of the C≡C bond. The ^{31}P-NMR spectrum reveals the alkyne coordination, since phosphorus resonances in complexes **9–11** are shifted nearly 25 ppm downfield with respect to those of the corresponding alkyne complex $[(Mp)Ph_2PC{\equiv}CR]^+$. This displacement is ascribed to the loss of the electron ring current associated with the $\pi(C{\equiv}C)$ bond [16] as a result of the alkyne coordination to the cobalt fragment. The carbonyl groups bonded to cobalt and molybdenum atoms are observed as separate signals in the ^{13}C-NMR spectra for complexes **9–11**. The carbonyl resonances of Mo–CO groups appear at about the same position as in the corresponding alkyne complexes $[(Mp)Ph_2PC{\equiv}CR)]^+$ and only the $^2J_{P\text{–}C}$ values for the Mo–CO(*cis*) are slightly lower. In addition, the carbonyl resonances of the Co–CO groups are observed as broad signals at nearly 198 ppm [17], in a position very similar to that previously reported for the iron–cobalt complexes $[(Fp)Ph_2PC_2R\{Co_2(CO)_6\}]^+$ [6]. Unfortunately, acetylenic carbon resonances were observed only for complex **10**, as two doublets at 84.6 ppm ($^1J_{PC} = 10.2$ Hz, P*C*≡) and 108.9 ppm ($^2J_{PC} = 7.7$ Hz, ≡*C*Ph). These chemical shifts are also very similar to those previously reported [6] for the homologous iron complex $[(Fp)Ph_2PC_2Ph\{Co_2(CO)_6\}]^+$ (84.7 and 107.7 ppm), so the electronic distribution of the acetylenic group should be similar in both complexes. Finally, the ^1H- and ^{13}C-NMR spectra show the resonances of Ph, Cp and R groups, with no exceptional chemical shifts.

The reaction between complex **3** and $[Co_2(CO)_8]$ did not lead to the corresponding cobalt complex, and the



R = CH_3(**9**), Ph(**10**), Tol(**11**)

Scheme 4.

reagents were recovered. This different behaviour is reported elsewhere [6], and can be assigned to the steric hindrance of the bulky *tert*-butyl group. In contrast, complex **1** showed similar behaviour to **2**, **4** and **5**, but the corresponding cobalt complex could not be isolated in an acceptable grade of purity.

3. Experimental

3.1. General

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin–Elmer 1710 FT spectrometer using dichloromethane solutions or KBr pellets. The NMR spectra were recorded by the Servei de Ressonancia Magnètica Nuclear de la Universitat Autònoma de Barcelona on a Bruker AM400 instrument. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvents for ^{1}H spectra, to solvent signals for ^{13}C spectra and to phosphoric acid for ^{31}P spectra.

Compounds $Ph_2PC{\equiv}CR$ (R = H, CH_3, ^{t}Bu, Ph, Tol, PPh_2) were prepared by published procedures [3,14a,18]. Microanalyses were performed in Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

*3.2. Synthesis of (**1**–**5**) {R = H (**1**), CH_3 (**2**), ^{t}Bu (**3**), Ph (**4**), Tol (**5**)}*

In a typical procedure, a solution of $Ph_2PC{\equiv}CR$ (2.1 mmol) in dicloromethane (5 ml) was added to a solution of $[CpMo(CO)_3]_2$ (0.500 g, 1.0 mmol) in dichloromethane (15 ml). Solid $AgBF_4$ (0.400 g, 2.0 mmol) was added and the reaction mixture was stirred at room temperature (r.t.) for 1 week. Next, solid silver was filtered off and the solution was evaporated to dryness. The residue was recrystallized from 2:1 CH_2Cl_2–diethyl ether at −20°C. The yellow crystals that separated were collected, washed in diethyl ether and dried in vacuo.

Yield of **1**: 62%. Anal. Calc. for $C_{22}H_{16}BF_4MoO_3P$: C, 48.75; H, 2.98. Found: C, 48.30; H, 2.90%. IR (CH_2Cl_2, cm^{-1}): 2065(s), 2005(m), 1976(s) (ν_{CO}). ^{1}H-NMR (acetone-d_6; except phenyl resonances): 5.32 (d, $^3J_{PH} = 12$ Hz, HC≡), 6.15 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): 23.3. ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 78.5 (d, $^1J_{PC} = 62.5$ Hz, ≡CP), 97.5 (Cp), 109.1 (d, $^2J_{PC} = 12.3$ Hz, ≡CH), 225.0 (d, $^2J_{PC} = 25.2$ Hz, CO_{cis}) 226.0 (s, CO_{trans}).

Yield of **2**: 68%. Anal. Calc. for $C_{23}H_{18}BF_4MoO_3P$: C, 49.68; H, 3.26. Found: 49.34; H, 3.42%. IR (CH_2Cl_2, cm^{-1}): 2202(m) ($\nu_{C\equiv C}$); 2063(s), 2003(m), 1975(s) (ν_{CO}).^{1}H-NMR (acetone-d_6; except phenyl resonances): 2.41 (d, $^4J_{PC} = 4.0$ Hz, CH_3), 6.11 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): 22.4. ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 5.2 (d, $^3J_{PC} = 3$ Hz, CH_3), 74.0 (d, $^1J_{PC} = 66.7$ Hz, ≡CP), 97.2 (Cp), 117.3 (d, $^2J_{PC} = 15.2$ Hz, ≡*C*Me), 225.4 (d, $^2J_{PC} = 30.4$ Hz, CO_{cis}) 226.8 (s, CO_{trans}).

Yield of **3**: 70%. Anal. Calc. for $C_{26}H_{24}BF_4MoO_3P$: C, 52.20; H, 4.04. Found: C, 51.44; H, 4.10%. IR (CH_2Cl_2, cm^{-1}): 2210(w), 2170(m) ($\nu_{C\equiv C}$); 2063(s), 2004(m), 1975(s) (ν_{CO}). ^{1}H-NMR (acetone-d_6; except phenyl resonances): 1.46 (s, ^{t}Bu), 6.10 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): 21.2. ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 24.3 (s, CH_3), 71.2 (d, $^1J_{PC} = 109.1$ Hz, ≡CP), 97.3 (Cp), 128.2 (d, $^2J_{PC} = 15.3$ Hz, ≡*C*-^{t}Bu), 225.8 (d, $^2J_{PC} = 27.8$ Hz, CO_{cis}) 226.6 (s, CO_{trans}).

Yield of **4**: 75%. Anal. Calc. for $C_{28}H_{20}BF_4MoO_3P$: C, 54.40; H, 3.26. Found: C, 54.41; H, 3.40%. IR (CH_2Cl_2, cm^{-1}): 2173(m) ($\nu_{C\equiv C}$); 2063(s), 2005(m), 1976(s) (ν_{CO}). ^{1}H-NMR (acetone-d_6; except phenyl resonances): 6.19 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): 22.8. ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 80.6 (d, $^1J_{PC} = 105.8$ Hz, ≡CP), 97.5 (Cp), 116.1 (d, $^2J_{PC} = 16.6$ Hz, ≡*C*Ph), 225.5 (d, $^2J_{PC} = 28.2$ Hz, CO_{cis}) 226.3 (s, CO_{trans}).

Yield of **5**: 64%. Anal. Calc. for $C_{29}H_{22}BF_4MoO_3P$: C, 55.10; H, 3.51. Found: C, 55.00; H, 3.67%. IR (CH_2Cl_2, cm^{-1}): 2172(m) ($\nu_{C\equiv C}$); 2063(s), 2004(m), 1973(s) ($_{CO}$). ^{1}H-NMR (acetone-d_6; except phenyl resonances): 2.44 (s, CH_3), 6.17 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): 22.8. ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 21.4 (s, CH_3), 79.8 (d, $^1J_{PC} = 110.0$ Hz, ≡CP), 97.3 (Cp), 116.7 (d, $^2J_{PC} = 18.6$ Hz, ≡*C*Ph), 225.4 (d, $^2J_{PC} = 30.0$ Hz, CO_{cis}), 226.3 (s, CO_{trans}).

*3.3. Synthesis of **6***

A solution of $Ph_2PC{\equiv}CPPh_2$ (0.480 g, 1.2 mmol) in dicloromethane (5 ml) was added to a solution of $[CpMo(CO)_3]_2$ (0.300 g, 0.6 mmol) in dichloromethane (15 ml). Solid $AgBF_4$ (0.240 g, 1.2 mmol) was added and the reaction mixture was stirred at r.t. for 1 week. Next, solid silver was filtered off and the solution was evaporated to dryness. The residue was recrystallized from 2:1 CH_2Cl_2–diethyl ether at −20°C. The yellow crystals that separated were collected, washed in diethyl ether and dried in vacuo.

Yield of **6**: 63%. Anal. Calc. for $C_{34}H_{25}BF_4MoO_3P_2$: C, 56.23; H, 3.47. Found: C, 56.42; H, 3.36%. IR (CH_2Cl_2, cm^{-1}): 2122(w) ($\nu_{C\equiv C}$); 2066(s), 2007(m), 1977(s) (ν_{CO}). ^{1}H-NMR (acetone-d_6; except phenyl resonances): 6.19 (s, Cp). ^{31}P{^{1}H}-NMR (acetone-d_6): −20.2 (b, PPh_2), 23.4 (b, Mo–PPh_2). ^{13}C{^{1}H}-NMR (acetone-d_6; except phenyl resonances): 96.5 (s, Cp), 224.6 (d, $^2J_{PC} = 25.2$ Hz, CO_{cis}), 225.1 (s, CO_{trans}) (the signals for acetylenic carbons could not be identified).

3.4. Synthesis of **7**

A solution of $Ph_2PC{\equiv}CPPh_2$ (0.240 g, 0.6 mmol) in dicloromethane (5 ml) was added to a solution of $[CpMo(CO)_3]_2$ (0.300 g, 0.6 mmol) in dichloromethane (15 ml). Solid $AgBF_4$ (0.24 g, 1.2 mmol) was added and the reaction mixture was stirred at r.t. for 1 week. Next, solid silver was filtered off and the solution was evaporated to dryness. The residue was recrystallized from 2:1 CH_3CN–diethyl ether at −20°C. The yellow crystals that separated were collected, washed in diethyl ether and dried in vacuo.

Yield of **7**: 65%. Anal. Calc. for $C_{42}H_{30}B_2F_8Mo_2O_6P_2$: C, 47.67; H, 2.86. Found: C, 47.02; H, 2.97%. IR (KBr, cm^{-1}): 2064(s), 2007(sh), 1970(s) (ν_{CO}). ^1H-NMR (CD_3CN; except phenyl resonances): 6.04 (s, Cp). $^{31}P\{^1H\}$-NMR (CD_3CN): 25.3. $^{13}C\{^1H\}$-NMR (CD_3CN; except phenyl resonances): 96.8 (s, Cp), 106.2 (dd, $^1J_{PC} = 72.5$, $^2J_{PC} = 3.8$ Hz, CP), 223.8 (d, $^2J_{PC} = 26.8$ Hz, CO_{cis}), 224.2 (s, CO_{trans}).

3.5. Synthesis of **8**

3.5.1. Method 1 (starting from complex **6**)

Solid complex **6** (0.350 g, 0.48 mmol) was added to a solution of $[CpFe(CO)_2]_2$ (0.086 g, 0.26 mmol) in dichloromethane (15 ml). The resulting solution was stirred for 5 min at r.t. and a solution of $[FeCp_2][BF_4]$ (0.130 g, 0.48 mmol) in dichloromethane (5 ml) was added. The solution was stirred at r.t. for 3 h, $FeCp_2$ filtered off, and evaporated to dryness. The residue was recrystallized from 2:1 CH_2Cl_2–diethyl ether at −20°C. The yellow crystals that separated were collected, washed in diethyl ether and dried in vacuo. Yield 65%.

3.5.2. Method 2 (starting from $[(Fp)Ph_2PC{\equiv}CPPh_2][BF_4]$)

Solid $[CpMo(CO)_3]_2$ (0.350 g, 0.7 mmol) and solid $AgBF_4$ (0.270 g, 1.4 mmol) were added to a solution of $[(Fp)Ph_2PC{\equiv}CPPh_2][BF_4]$ (0.900 g, 1.4 mmol) in dichloromethane (15 ml) and the reaction mixture was stirred at r.t. for 1 week. Next, solid silver was filtered off and the solution was evaporated to dryness. The residue was recrystallized from 2:1 CH_2Cl_2–diethyl ether at −20°C. The yellow crystals that separated were collected, washed in diethyl ether and dried in vacuo. Yield 57%.

Anal. Calc. for $C_{41}H_{30}B_2F_8FeMoO_5P_2$: C, 49.74; H, 3.05. Found: C, 49.29; H, 3.20%. IR (CH_2Cl_2, cm^{-1}): 2065(s), 2022(s), 1978(s) (ν_{CO}). IR (KBr, cm^{-1}): 2122(w) ($\nu_{C\equiv C}$). ^1H-NMR (acetone-d_6; except phenyl resonances): 5.76 (s, CpFe), 6.11 (s, CpMo). $^{31}P\{^1H\}$-NMR (acetone-d_6): 24.7(s, PMo), 46.7(s, PFe). $^{13}C\{^1H\}$-NMR (acetone-d_6; except phenyl resonances): 89.9 (s, CpFe), 97.3 (s, CpMo), 208.6 (d, $^2J_{PC} = 22.5$ Hz, FeCO), 224.1 (d, $^2J_{PC} = 26.8$ Hz, $MoCO_{cis}$), 225.3 (s, $MoCO_{trans}$) (the signals for acetylenic carbons could not be identified).

3.6. Synthesis of **9**–**11** {R = CH_3 (**9**), Ph (**10**), Tol (**11**)}

In a typical procedure, a solution of $[Co_2(CO)_8]$ (0.110 g, 0.32 mmol) in dicloromethane (15 ml) was added with stirring to $[(Mp)Ph_2PC{\equiv}CR][BF_4]$ (0.32 mmol) in dichloromethane (15 ml). The solution was stirred at r.t. for 20 h, filtered, and evaporated to dryness. The residue was recrystallized from 1:1 CH_2Cl_2–diethyl ether at −20°C. The brown crystals that separated were collected, washed in diethyl ether and dried in vacuo.

Yield of **9**: 75%. Anal. Calc. for $C_{29}H_{18}BCo_2F_4MoO_9P$: C, 41.37; H, 2.15. Found: C, 41.37; H, 2.34%. IR (CH_2Cl_2, cm^{-1}): 2101(m), 2067(s), 2045(s), 2010(m) 1963(m) (ν_{CO}). ^1H-NMR (acetone-d_6; except phenyl resonances): 3.28 (s, CH_3), 5.95 (s, Cp). $^{31}P\{^1H\}$-NMR (acetone-d_6): 47.7. $^{13}C\{^1H\}$-NMR (acetone-d_6; except phenyl resonances): 23.3 (s, CH_3), 96.7 (s, Cp), 198.1 (b, CoCO), 226.6 (s, CO_{trans}) 227.9 (d, $^2J_{PC} = 25.0$ Hz, CO_{cis}) (the signals for acetylenic carbons could not be identified).

Yield of **10**: 75%. Anal. Calc. for $C_{34}H_{20}BCo_2F_4MoO_9P$: C, 45.17; H, 2.23. Found: C, 44.79; H, 2.37%. IR (CH_2Cl_2, cm^{-1}): 2103(m), 2070(s), 2050(s), 2020(m) 1969(m) (ν_{CO}). ^1H-NMR (acetone-d_6; except phenyl resonances): 5.87 (s, Cp). $^{31}P\{^1H\}$-NMR (acetone-d_6): 47.5. $^{13}C\{^1H\}$-NMR (acetone-d_6; except phenyl resonances): 84.6 (d, $^1J_{PC} = 10.2$ Hz, $CPPh_2$), 97.4 (s, Cp), 108.9 (d, $^2J_{PC} = 7.7$ Hz, CPh), 198.6 (b, CoCO), 225.4 (s, CO_{trans}), 227.9 (d, $^2J_{PC} = 25.7$ Hz, CO_{cis}).

Yield of **11**: 72%. Anal. Calc. for $C_{35}H_{22}BCo_2F_4MoO_9P$: C, 45.79; H, 2.42. Found: C, 45.47; H, 2.44%. IR (CH_2Cl_2, cm^{-1}): 2098(m), 2065(s), 2036(s), 2022(m) 1975(m) (ν_{CO}). ^1H-NMR (acetone-d_6; except phenyl resonances): 2.40 (s, CH_3), 5.89 (s, Cp). $^{31}P\{^1H\}$-NMR (acetone-d_6): 47.5. $^{13}C\{^1H\}$-NMR (acetone-d_6; except phenyl resonances): 22.6 (s, CH_3), 96.7 (s, Cp), 198.0 (b, CoCO), 226.2 (s, CO_{trans}), 227.2 (d, $^2J_{PC} = 23.2$ Hz, Co_{cis}) (the signals for acetylenic carbons could not be identified).

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