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Multisite Reactivity of the Central Mo_2CP Core in the Unsaturated Carbyne-Bridged Complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$

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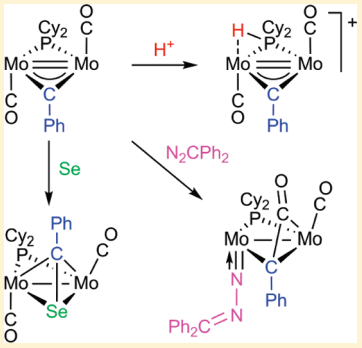
Supporting Information

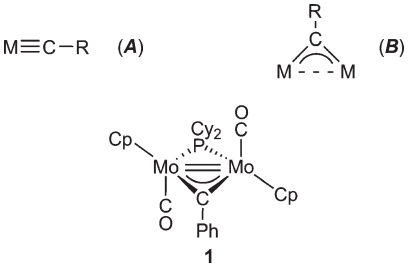
ABSTRACT: The title compound reacted with $HBF_4 \cdot OEt_2$ at room temperature to give a mixture of the agostic-like, phosphine-bridged complex $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}\kappa^1\text{:}\eta^2\text{-}PHCy_2)(CO)_2]BF_4$ (major) and the carbene-bridged complex $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CHPh)(\mu\text{-}PCy_2)(CO)_2]BF_4$ (minor). It readily added a molecule of $HC{\equiv}CCO_2Me$ or a single Se atom at its Mo_2C(carbyne) center to give with high yield the corresponding propenylylidene- or selenoacyl-bridged derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}CPhCHC(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ and $[Mo_2Cp_2\{\mu\text{-}\eta,\kappa\text{:}\eta,\kappa\text{-}C(Ph)Se\}(\mu\text{-}PCy_2)(CO)_2]$, respectively. In contrast, the addition of a neat donor at the metal site can induce a reversible carbyne−carbonyl coupling, as observed in the reaction with N_2CPh_2 to give the ketenyl derivative $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$.



The chemistry of carbyne complexes is an intensively studied area within organometallic science. These compounds usually display a high reactivity derived from the multiple nature of their metal−carbon bonds in either the terminal or the edge-bridging coordination modes (***A*** and ***B*** in Chart 1),[1] and they are also involved in several industrial processes of interest such as the Fischer−Tropsch (FT) synthesis of hydrocarbons from syngas ($CO + H_2$)[2] and alkyne metathesis.[3] The reactivity of the edge-bridged complexes can be further increased by the presence of multiple metal−metal bonds. Moreover, the chemistry of a carbyne ligand at such unsaturated dimetal centers can be considered as a crude but simple model of the chemical behavior of related surface species formed in different heterogeneously catalyzed reactions, notably the C−C coupling processes involved in the FT synthesis. Indeed, our previous studies on the behavior of the unsaturated methoxycarbyne-bridged complexes $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$[4] and $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2]$[5] revealed a high and multipositional reactivity of these electron-deficient dimetal centers under mild conditions, including some interesting C−C bond formation processes.[4d,5c]

Recently we described efficient synthetic procedures for the preparation of the unsaturated benzylidyne complexes $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ and $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$,[6] which are structurally and electronically related to the mentioned methoxycarbyne complexes, this providing an ideal opportunity to compare the multisite reactivity of all these unsaturated carbyne complexes. Initial studies on the chemical behavior of the 30-electron monocarbonyl complex revealed the involvement of the carbyne ligand in unusual C−C and C−P coupling processes, but only at cationic derivatives following alkylation or oxidation steps.[7] In its neutral state, this molecule seems to be rather unreactive toward small unsaturated organic molecules such as alkynes or diazoalkanes. We then turned our attention to the 32-electron complex $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$ (**1**), which has a dimetal core bridged by only two ligands and therefore is more accessible to external reagents (Chart 1). In this paper we report our preliminary studies on the reactions of **1** with different reagents ranging from protonic acids or small unsaturated organic molecules such as alkynes and diazoalkanes to simple elements such as chalcogens (Scheme 1). From this we conclude that compound **1** is more reactive than the triply bridged $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ as anticipated, but also that this dicarbonyl complex displays a multisite reactivity that is somewhat unexpected since all elements of the central Mo_2CP core can be involved in these reactions, that is, not only the Mo−Mo and Mo−C bonds, but also the Mo−P bonds of the dicyclohexylphosphide bridge.

Chart 1



Compound **1** is basic enough to be protonated by strong acids such as $HBF_4 \cdot OEt_2$. However, this reaction unexpectedly gives a

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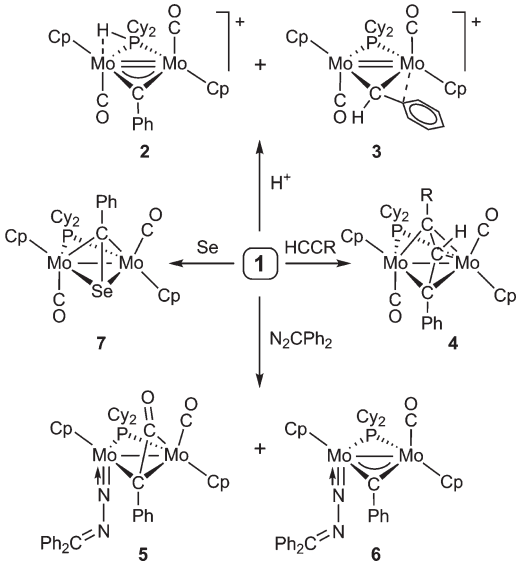
Scheme 1



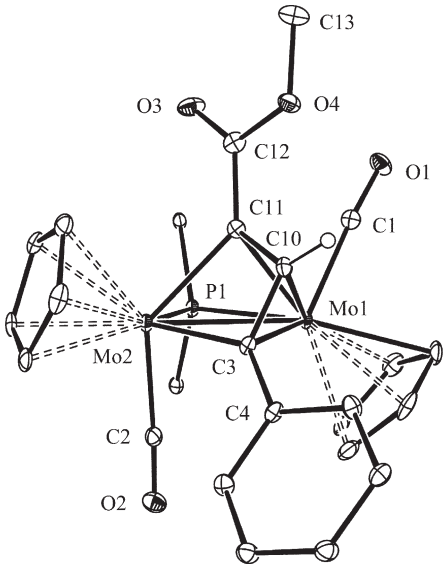


Figure 1. ORTEP drawing (30% probability) of compound **4**, with H atoms (except H10) and cyclohexyl rings (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.8349(5), Mo1−P1 = 2.475(1), Mo1−C1 = 1.971(5), Mo1−C3 = 2.399(4), Mo1−C10 = 2.279(5), Mo1−C11 = 2.198(5), Mo2−P1 = 2.416(1), Mo2−C2 = 1.991(5), Mo2−C3 = 2.184(4), Mo2−C11 = 2.193(5), C3−C10 = 1.402(6), C10−C11 = 1.446(6), C11−C12 = 1.458(7), C12−O3 = 1.210(6), C12−O4 = 1.350(6); Mo2−Mo1−C1 = 117.9(1), Mo1−Mo2−C2 = 84.0(1).

mixture of two quite air-sensitive products when carried out in dichloromethane solution at room temperature (Scheme 1): the agostic-like, phosphine-bridged complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-}\kappa^1\text{:}\eta^2\text{-PHCy}_2)(CO)_2]BF_4$ (**2**)[8] and the carbene-bridged complex $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CHPh})(\mu\text{-PCy}_2)(CO)_2]BF_4$ (**3**).[9] Although we have not been able to separate these products by fractional crystallization so far, the phosphine complex **2** could be obtained as an essentially pure material by carrying out the protonation reaction at 243 K, thus facilitating the spectroscopic characterization of these products. Moreover we note that compound **2** does not transform into **3** at room temperature or even upon warming it at ca. 323 K in dichloromethane solution.

The formation of **2** follows from the protonation of the neutral substrate **1** at a Mo−P bond of the bridging PCy_2 ligand, an unusual and orbital-controlled reaction recently described by us for isoelectronic complexes of the type $[Mo_2Cp_2(\mu\text{-PR}_2)(\mu\text{-PR'}_2)(CO)_2]$ having electron-rich PR_2 bridges, to give the corresponding cations $[Mo_2Cp_2(\mu\text{-PR'}_2)(\mu\text{-}\kappa^1\text{:}\eta^2\text{-PHR}_2)(CO)_2]^+$.[5b,10] Indeed, a DFT calculation on the related carbyne complex $[Mo_2Cp_2\{\mu\text{-C(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ indicates that the HOMO−4 orbital in this molecule has a large Mo−P σ-bonding character,[5a] thus pointing to the formation of **2** as an orbital-controlled event. In contrast, the mentioned calculation reveals a significant negative charge at the carbyne C atom, thus suggesting that the formation of the carbene complex **3** would be favored on electrostatic grounds. The presence of the agostic-like Mo−H−P interaction in **2** is denoted by the appearance of relatively shielded ^{31}P and ^1H NMR resonances (131.4 and −4.30 ppm, respectively) with strongly reduced one-bond mutual coupling (117 Hz), that is, about half the usual values for comparable "normal" P−H bonds.[10] For complex **3**, the appearance in the ^{13}C NMR spectrum of a relatively shielded CH resonance at 180 ppm denotes the transformation of the former carbyne ligand into a bridging carbene group. Although the formation of the latter ligand in principle would reduce the electron count of the dimetal center and thus would increase its electronic unsaturation, there is no evidence of an agostic C−H interaction of the carbene ligand with the dimetal center to mitigate such an unsaturation. Instead, we note that the *ipso* resonance of the phenyl ring is considerably shielded (δ_C 115.2 ppm), this being taken as a piece of evidence for the coordination of at least that carbon atom to one of the molybdenum atoms ($\mu\text{-}\eta^1\text{:}\eta^2$-mode, Scheme 1). We note that a few arylcarbene complexes exhibiting closely related interactions of the *ipso* and *ortho* carbons of their aryl rings ($\mu\text{-}\eta^1\text{:}\eta^3$-mode) have been structurally characterized previously.[11] The protonation reactions of the unsaturated complex **1** just discussed share some analogies, but also significant differences, with the analogous reactions of the electron-precise alkylidyne complexes $[Mo_2Cp_2(\mu\text{-CH}_2\text{R})(\mu\text{-SMe})_3]$ (R = 4-Me-C_6H_4, *n*-Pr).[12] In fact, the latter reactions give alkylidene derivatives displaying agostic C−H···Mo (instead of C−C···Mo) interactions when carried out in dichloromethane solutions, but they result in the loss of an HSMe molecule when carried out in acetonitrile solution.[12c]

The unsaturated nature and relatively unprotected central Mo_2PC core of **1** facilitates the addition of small unsaturated molecules such as alkynes and diazoalkanes, as well as some concomitant C−C coupling processes. For instance, compound **1** reacts with methyl propiolate at 333 K to give with high yield the corresponding propenylylidene derivative $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^3\text{-CPhCHC(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (**4**) resulting from the specific coupling of the carbyne ligand to the terminal carbon of the alkyne.[13] This behavior parallels that previously observed for the isoelectronic methoxycarbyne complex $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(CO)_2]$[5c] and the heterometallic complex $[FeMoCp\{\mu\text{-C}(p\text{-tol})\}(CO)_5]$.[14] In the crystal (Figure 1),[15] the intrinsic asymmetry of the bridging hydrocarbyl ligand (providing the Mo1 atom with one more electron) is balanced by a tighter binding of the P and C3 atoms to Mo2.

In contrast, the addition of a molecule of N_2CPh_2 to the unsaturated compound **1** induces a C−C coupling process of the

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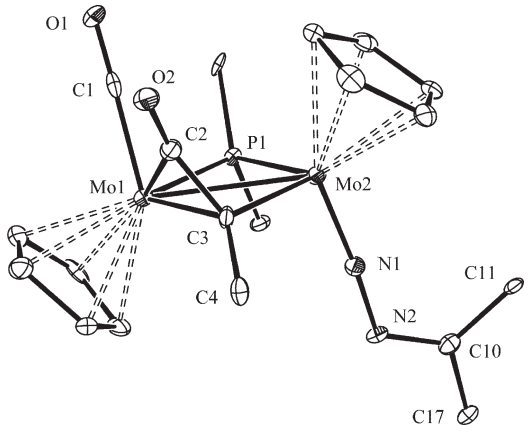

Figure 2. ORTEP drawing (30% probability) of compound **5**, with H atoms and cyclohexyl and phenyl rings (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.8935(9), Mo1−P1 = 2.364(2), Mo1−C1 = 1.932(8), Mo1−C2 = 2.163(7), Mo1−C3 = 2.203(7), Mo2−P1 = 2.432(2), Mo2−C3 = 2.148(7), Mo2−N1 = 1.748(5), N1−N2 = 1.338(7), N2−C10 = 1.306(8), C3−C2 = 1.398(9), C2−O2 = 1.215(8); Mo2−Mo1−C1 = 96.4(2), Mo1−Mo2−N1 = 103.6(2). Mo2−N1−N2 = 174.6(5), N1−N2−C10 = 120.0(6), C3−C2−O2 = 142.3(7), Mo1−C2−O2 = 144.2(5).

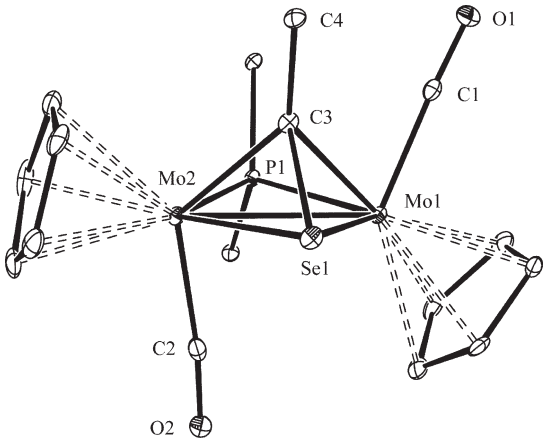

Figure 3. ORTEP drawing (30% probability) of compound **7**, with H atoms and cyclohexyl and phenyl rings (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.8950(3), Mo1−P1 = 2.4415(6), Mo1−C1 = 1.921(2), Mo1−C3 = 2.180(2), Mo1−Se1 = 2.5611(3), Mo2−P1 = 2.4084(6), Mo2−C2 = 1.977(2), Mo2−C3 = 2.121(2), Mo2−Se1 = 2.5916(3); Se1−C3 = 1.924(2), Mo2−Mo1−C1 = 113.0(1), Mo1−Mo2−C2 = 79.5(1).

carbyne with a carbonyl ligand, rather than a coupling with the added reagent. Actually, this reaction takes place only at very high concentrations and gives a mixture of two diazoalkane complexes: the ketenyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**5**)[16] and its carbyne derivative $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**6**).[17] Independent experiments revealed that these species are related by carbonylation/decarbonylation processes, therefore allowing their selective preparation. Thus, the above mixture can be transformed into pure **5** by reacting it with CO (ca. 3 atm) in dichloromethane solution at room temperature. In contrast, heating at 353 K a toluene solution of this mixture for 30 min yields pure compound **6** (see the Supporting Information). The formation of **5** gives experimental support to our previous hypothesis that the formation of the ketenyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)_2]$ upon carbonylation of **1** would imply the coordination of CO to the unsaturated dimetal center of **1** followed by reorganization, rather than arising from direct attack of CO to the electron-rich carbyne ligand.[6]

The geometrical parameters of the terminal diazoalkane ligand in **5** (Figure 2)[18] indicate that this group acts as a four-electron donor (imido-like coordination) to the dimetal center,[19] and this is balanced by an asymmetric coordination ($\mu\text{-}\eta^1\text{:}\eta^2$ mode) of the ketenyl ligand, in turn acting as a three-electron donor. As a result, the molecule formally is electron-precise, as found previously for the related diphenylphosphide complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(\kappa^1\text{-}N_2CPh_2)]$,[20] and this is in agreement with the relatively large intermetallic length of ca. 2.90 Å. The same comment applies to compound **6**, except that the ketenyl ligand is here being replaced by a bridging carbyne, as denoted by the presence in its ^{13}C NMR spectrum of a strongly deshielded resonance at 373.5 ppm. We finally note that the asymmetric coordination mode of the ketenyl ligand found in **5** has been previously characterized in a few, usually heterometallic substrates,[21] the only homometallic precedent being the ditungsten complex $[W_2(\mu\text{-}Br)Br_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(4\text{-}Me\text{-}C_6H_4)CO\}(CO)\{\mu\text{-}F_2PN(Me)PF_2\}_2]$.[21a]

The unsaturated nature of **1** also facilitates the addition under mild conditions of single chalcogen atoms to the central Mo_2C triangle to give symmetrically bridging ($\mu\text{-}\eta,\kappa\text{:}\eta,\kappa$ mode) chalcoacyl ligands, thus paralleling the behavior of related heterometallic complexes of the type $[MFeL(\mu\text{-}CR)(CO)_x]$ toward elemental S and Se (M = Mo, W; L = Cp or related ligand; R = *p*-tol, Xyl; *x* = 5, 6).[22] For instance, compound **1** reacts with gray selenium at 333 K to give the selenoacyl derivative $[Mo_2Cp_2\{\mu\text{-}\eta,\kappa\text{:}\eta,\kappa\text{-}C(Ph)Se\}(\mu\text{-}PCy_2)(CO)_2]$ (**7**) almost quantitatively.[23] In the crystal (Figure 3),[24] the selenioacyl ligand displays single-bond lengths of ca. 2.58 Å (Se−Mo) and 2.15 Å (C3−Mo) to both metal atoms. These values are comparable to those recently measured for the heterometallic complex $[MoRh\{\mu\text{-}\eta,\kappa\text{:}\eta,\kappa\text{-}C(R)Se\}Cl(CO)_2(PPh_3)\{HB(pzMe_2)_3\}]$ (R = C_2SiMe_3), which appears to be the only other selenoacyl-bridged complex structurally characterized so far.[25] As a result of this coordination mode, the selenoacyl ligand in **7** acts as a five-electron donor to the dimetal center, which then becomes electron-precise, in agreement with the measured intermetallic distance of ca. 2.90 Å.

In summary, we have shown that the unsaturated benzyliyne complex **1** displays a multisite reactivity of its central Mo_2PC core involving not only the addition of neat electron donors at the electron-deficient metal site (reaction with N_2CPh_2) or the addition of ambiphilic reagents to the Mo_2C face (reactions with selenium and $HC{\equiv}CCO_2Me$) but also the addition of neat acceptors either at the carbyne atom or at the Mo−P bonds (protonation reaction). Further studies are now in progress to fully explore the synthetic potential of this 32-electron carbyne-bridged dimolybdenum complex.

■ ASSOCIATED CONTENT

Supporting Information. Text giving experimental procedures and spectroscopic and microanalytical data for new compounds (PDF) and a CIF file giving crystallographic data for compounds **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Selected data for **2**: ν(CO) (CH_2Cl_2): 1981 (w), 1958 (vs) cm^{-1}. ^1H NMR (400.13 MHz, CD_2Cl_2): δ −4.30 (d, J_{PH} = 117, μ-PH). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ 131.4. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 253 K): δ 415.3 (s, μ-CPh).

(9) Selected data for **3**: ν(CO) (CH_2Cl_2): 1981 (w), 1958 (vs) cm^{-1}. ^1H NMR (400.13 MHz, CD_2Cl_2, 213 K): δ 9.18 (s, 1H, μ-CH). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2, 213 K): δ 214.8. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 213 K): δ 180.0 (s, μ-CHPh), 115.2 [s, C^1(Ph)].

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(13) Selected data for **4**: ν(CO) (CH_2Cl_2): 1916 (m), 1886 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2): δ 140.3. $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2): δ 137.7 (s, μ-CPh), 92.1 (d, J_{CP} = 5, MoCH), 78.4 (d, J_{CP} = 28, μ-CCO_2Me).

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(15) X-ray data for **4**: orange crystals, triclinic ($P\bar{1}$), a = 9.8540(5) Å, b = 11.4584(6) Å, c = 16.1062(8) Å, α = 76.032(3)°, β = 79.622(4)°, γ = 81.141(3)°, V = 1724.3(2) $Å^3$, T = 100 K, Z = 2, R = 0.0551 (observed data with $I > 2\sigma(I)$), GOF = 1.031.

(16) Selected data for **5**: ν(CO) (CH_2Cl_2): 1864 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2): δ 216.4. $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2): δ 234.4 (d, J_{CP} = 12, MoCO), 226.0 [s, MoC(O)], 136.5 (s, N_2CPh_2), 134.4 (s, μ-CPh).

(17) Selected data for **6**: ν(CO) (CH_2Cl_2): 1872 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ 188.7. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): δ 373.5 (d, J_{CP} = 6, μ-CPh), 248.5 (d, J_{CP} = 10, MoCO), 133.9 (s, N_2CPh_2).

(18) X-ray data for **5**: green crystals, triclinic ($P\bar{1}$), a = 9.6616(13) Å, b = 14.445(2) Å, c = 16.173(2) Å, α = 93.467(9)°, β = 97.332(8)°, γ = 105.068(8)°, V = 2151.4(5) $Å^3$, T = 100 K, Z = 2, R = 0.0715 (observed data with $I > 2\sigma(I)$), GOF = 1.021.

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(23) Selected data for **7**: ν(CO) (THF): 1889 (sh), 1872 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2): δ 124.3. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 253 K): δ 89.6 (s, μ-CSe).

(24) X-ray data for **7**: brown crystals, monoclinic ($P2_1/c$), a = 10.0964(4) Å, b = 15.8350(6) Å, c = 21.7892(8) Å, β = 115.617(2)°, V = 3141.2(2) $Å^3$, T = 100 K, Z = 4, R = 0.0428 (observed data with $I > 2\sigma(I)$), GOF = 1.039.

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