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Phosphinidenes

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Enhanced Nucleophilic Behavior of a Dimolybdenum Phosphinidene Complex: Multicomponent Reactions with Activated Alkenes and Alkynes in the Presence of CO or CNXyl**

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In memory of F. Gordon A. Stone

Transition-metal complexes containing carbene ligands (CR_2) show high versatility for the synthesis of carbo- and heterocycles, and are key species with relevant roles in biochemistry, organic synthesis, and catalysis, including the metathesis, dimerization, polymerization, and oxidation of olefins.[1] Phosphinidene ligands (PR) are the phosphorus analogues of carbenes,[2] and their metal complexes are particularly attractive synthons for the design of phosphaorganic molecules displaying low-coordinate phosphorus centers.[3] As is the case with their carbene counterparts, phosphinidene complexes can be roughly divided into electrophilic (Fischer type)—displaying reactivity comparable to that of singlet carbenes—and nucleophilic (Schrock type)—displaying a phospha-Wittig reactivity.[2,3] This chemistry has been an exciting area of research since the early observations of cycloaddition reactions of transient electrophilic phosphinidene complexes with alkenes and alkynes to form coordinated phosphiranes and phosphirenes.[3,4] In contrast with the latter behavior, nucleophilic complexes have been shown instead to undergo [2+2] cycloaddition with alkynes, and even with alkenes in a few instances, to give phosphametallacycles.[3c,5] Notably, this chemistry has been developed mainly using mononuclear complexes, while the chemistry of phosphinidene-bridged binuclear complexes has been comparatively little explored until recently,[6,7] in spite of the diverse behavior that it might be anticipated for the different coordination modes of the PR ligands in binuclear environments (**A** to **C** in Figure 1). Recent studies on the ditungsten carbonyl complex $[W_2(\mu\text{-}PCp^*)(CO)_{10}]$ (type **A**; $Cp^* = C_5Me_5$) have revealed marked electrophilic behavior of the phosphinidene ligand,[6a,b] and the same can be said of the dimanganese complex $[Mn_2(\mu\text{-}PR)(CO)_8]$ ($R = N\mathit{i}Pr_2$, tetramethylpiperidyl).[6f,g] In contrast, our own studies on binuclear cyclopentadienyl/carbonyl complexes of iron (type **C**) and molybdenum (types **A** and **B**) reveal that these molecules can display reactivity patterns reminiscent of both the nucleophilic and the electrophilic mononuclear complexes, which makes them very promising synthetic intermediates.[7]

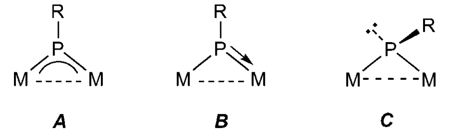
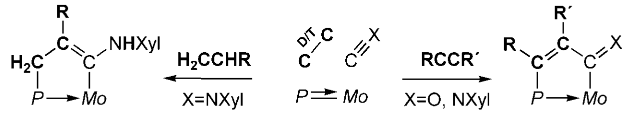


Figure 1. Coordination modes of the PR ligand at dimetal centers.

In the course of our studies on the reactivity of the type **B** dimolybdenum complex $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2L]$ (**1**) ($Cp = \eta^5\text{-}C_5H_5$; $L = \eta^6\text{-}1,3,5\text{-}\mathit{t}Bu_3C_6H_3$) we found that this compound failed to react with alkenes and alkynes at room temperature, but reacted with alkynes in refluxing toluene solutions to give products resulting from a [2+2] cycloaddition of the alkyne to the multiple Mo–P bond of the phosphinidene complex.[7f] This result is reminiscent of the behavior of nucleophilic mononuclear phosphinidene complexes,[3b,5a–c] and also of some mononuclear phosphide complexes.[8]

In contrast, we report herein that, in the presence of CO or CNXyl ligands ($Xyl = 2,6\text{-}C_6H_3Me_2$), compound **1** is able to react rapidly at room temperature with several electron-poor alkynes and alkenes, which results in a multicomponent reaction (MCR) to yield cycloaddition products having novel five-membered phosphametallacycles resulting from highly selective coupling between the alkyne/alkene, the added ligand, and the Mo–P multiple bond of the substrate **1** (Schemes 1 and 2). These reactions, themselves related to the MCR synthesis of heterocyclic organic compounds,[9] are unprecedented in the chemistry of isolable phosphinidene complexes, and perhaps they might be extended in the near future to other combinations of small organic molecules. We note, however, that a few related MCRs involving transient phosphinidene-derived mononuclear complexes have been reported, although the selectivity and yields are far lower than those reported herein.[10]



Scheme 1. Multicomponent reactions described in this work.

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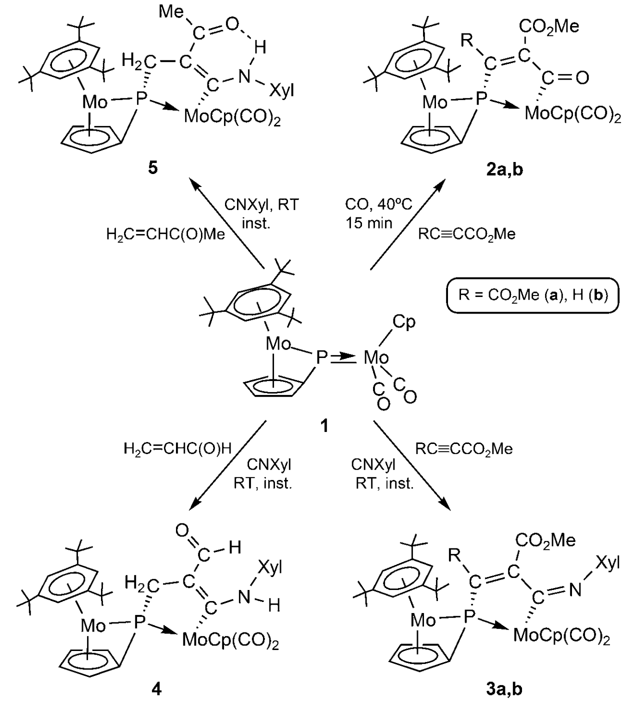


Scheme 2. Syntheses of compounds **2**–**5**.

Compound **1** reacts smoothly with dimethyl acetylenedicarboxylate or methyl propiolate, in the presence of CO, to give the corresponding phosphide–acyl derivatives $[\mathrm{Mo_2Cp}\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(\mathrm{C_5H_4})\mathrm{PCR=C(CO_2Me)C(O)}\}(\mathrm{CO})_2\mathrm{L}]$ (R = $\mathrm{CO_2Me}$ (**2a**), H (**2b**)) as sole products.[11] In the presence of 2,6-dimethylphenyl isocyanide (CNXyl), however, related but instantaneous reactions take place to give the corresponding phosphide–iminoacyl derivatives $[\mathrm{Mo_2Cp}\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(\mathrm{C_5H_4})\mathrm{PCR=C(CO_2Me)C(NXyl)}\}(\mathrm{CO})_2\mathrm{L}]$ (R = $\mathrm{CO_2Me}$ (**3a**), H (**3b**)). We note that in these reactions the addition of the C–C multiple bond to yield a phosphametallacyclopentene ring occurs in a highly regio- and chemoselective way, whereby the P atom is bound to the less substituted C atom of the alkyne.

Compound **1** also reacts instantaneously with electron-poor alkenes such as $\mathrm{H_2C{=}CHC(O)H}$ and $\mathrm{H_2C{=}CHC(O)Me}$ in the presence of CNXyl to give the corresponding phosphametallacyclopentene complexes $[\mathrm{Mo_2Cp}\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(\mathrm{C_5H_4})\mathrm{PCH_2CR=C(NHXyl)}\}(\mathrm{CO})_2\mathrm{L}]$ (R = C(O)H (**4**), C(O)Me (**5**)). These reactions also involve an [1,3]-H sigmatropic rearrangement to yield the corresponding enylamine grouping, and take place in a highly chemo- and regioselective way as well.

Compounds **2** to **5** were fully characterized in solution by IR and NMR spectroscopic techniques,[11] and also in the solid state by single-crystal X-ray diffraction studies on **2a** and **4** (Figures 2 and 3).[12] In the crystal, the latter complexes display similar geometries, except for the relative conformation of the $\mathrm{MoCp(CO)_2}$ fragment, implying an *anti* arrangement of the $\mathrm{C_5H_5}$ and $\mathrm{C_5H_4}$ rings in **2a** (as found in the precursor **1**), but a *syn* one in the case of **4**. The mentioned *cis*-dicarbonylic Mo fragment has a four-legged piano stool local environment completed by the phosphorus atom and the C atom of the acyl or enylamine group, respectively. In both cases the P atom displays an unusual distorted trigonal pyramidal (rather than tetrahedral) environment with the $\mathrm{PMo_2C5}$ (**2a**) or $\mathrm{PMo_2C3}$ (**4**) atoms almost in the same plane (sum of angles 358.7° and 360° respectively) and the *ipso* carbon atom of the $\mathrm{C_5H_4}$ ring placed in the apical position. This structural feature has been previously found in several heterometallic derivatives of compound **1**, and it is thought to be caused by a combination of steric effects and the geometrical constraints derived from the bifunctional coordination of the $\mathrm{C_5H_4P}$ ligand.[7c] As observed for the mentioned heterometallic derivatives, the P–Mo bonds involving the metallocene fragment (ca. 2.55 Å) are considerably longer than the corresponding length in **1** (2.403(1) Å).[7f] In contrast, the Mo–P (ca. 2.46 Å) and Mo–C (ca. 2.23 Å) bonds within the phosphametallacycle rings have comparable lengths to those determined for mononuclear phosphine–acyl complex $[\mathrm{MoCp}\{\mathrm{Ph_2PCH{=}CPhC(O)}\}(\mathrm{CO})_2]$ (2.467(2) and 2.273(3) Å, respectively).[13]

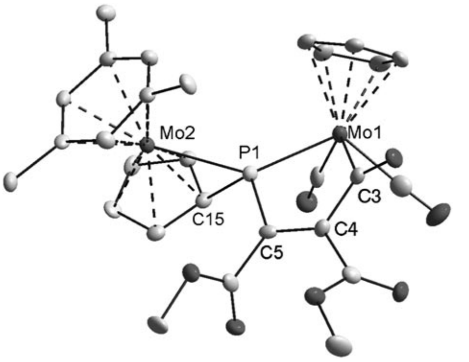


Figure 2. Diamond plot of the structure of **2a** in the crystal with ellipsoids at 50% probability and ring H atoms and Me groups of *t*Bu groups omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–P1 2.474(1), Mo2–P1 2.557(1), Mo1–C3 2.211(5), C3–C4 1.518(7), C3–O3 1.221(6), C4–C5 1.343(6), P1–C5 1.820(5); C4-C5-P1 112.8(4), C5-C4-C3 118.7(4), Mo1-P1-Mo2 136.8(1), C5-P1-Mo2 117.0(2), C5-P1-Mo1 105.0(2), C15-P1-Mo2 57.3(2).

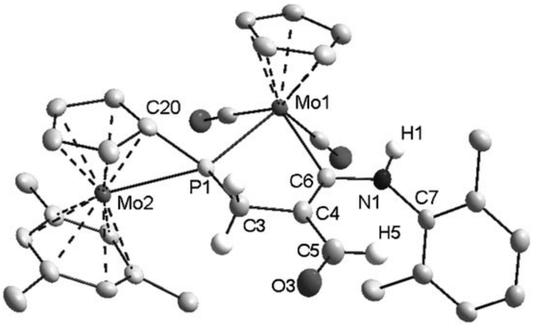


Figure 3. Diamond plot of the structure of **4** in the crystal with ellipsoids at 50% probability and ring H atoms and Me groups of *t*Bu groups omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–P1 2.453(1), Mo2–P1 2.557(1), Mo1–C6 2.259(3), C6–C4 1.388(5), C4–C3 1.511(4), P1–C3 1.838(3), C6–N1 1.377(4), C7–N1 1.432(4); C4-C3-P1 108.4(2), C5-C4-C3 113.4(3), Mo1-P1-Mo2 140.4(1), C3-P1-Mo2 114.3(1), C3-P1-Mo1 105.4(1), C6-N1-C7 131.4(3), C6-N1-H1 116(2), C7-N1-H1 113(2).

The P1, C5, C4, and C3 atoms of the metallacyclic ring in **2a** are coplanar (mean deviation from the least-squares plane 0.010 Å) and the C3–C4 and C4–C5 separations (1.518(7) Å and 1.343(6) Å) are appropriate for single and double C–C bonds respectively, with the latter value being slightly shorter than the corresponding one within the four-membered metallacycle of the complex [$Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5:\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)\}(CO)_2L$] (1.352(4) Å),[7f] and comparable to that in the mononuclear complex [$MoCp\{Ph_2PCH{=}CPhC(O)\}(CO)_2$] (1.337(4) Å).[13] In compound **4**, however, the short C4–C6 distance is somewhat longer (1.388(5) Å), which suggests some resonance contribution from the exocyclic NHXyl group. In line with this result, the environment around the N atom is planar, and the N1–C6 distance (1.377(4) Å) is shorter than the N1–C7 one (1.432(4) Å), although these values are in any case consistent with C(sp^2)–N single bonds (ca. 1.38 Å).[14] Notably, the orientation of the xylyl and aldehyde substituents allow a close approach of the C(O)H proton to the centroid (*X*) of the xylyl ring, with geometrical parameters (H5···*X* 2.767 Å; C-H5···*X* 155.9°], which are indicative of a significant intramolecular C–H···π interaction.[15] Moreover, the *syn* arrangement of the C_5H_5 and C_5H_4 rings in **4** also facilitates the pair wise self-assembly of molecules in the crystal (Figure 4) held by strong intermolecular π···π stacking interactions,[16] with the closest inter-ring distances of approximately 3.29 Å being slightly shorter than the interlaminar spacing in graphite (ca. 3.35 Å).

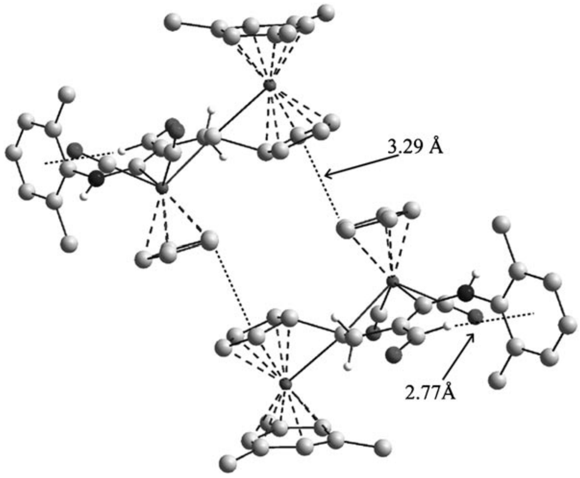


Figure 4. C–H···π and π···π stacking interactions in compound **4**.

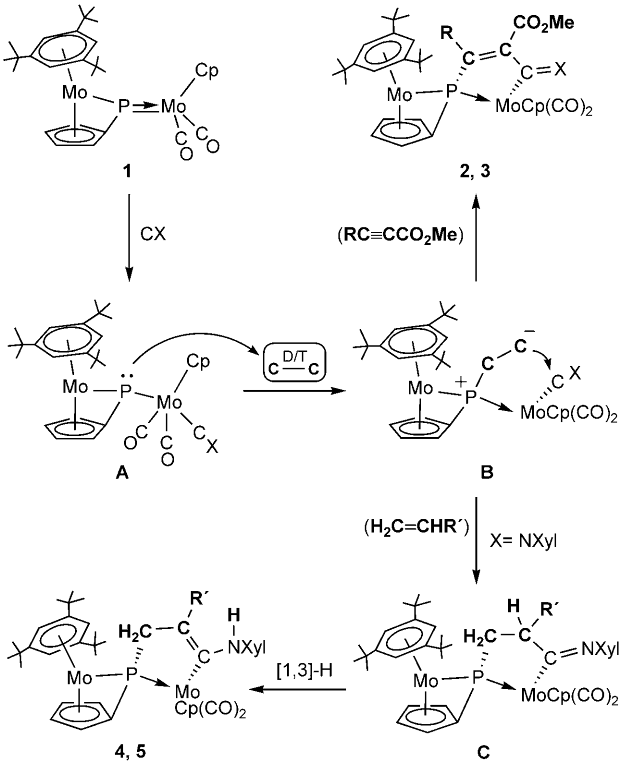
In solution, compounds **2a** and **2b** exist as mixtures of the corresponding *syn* (minor) and *anti* (major) isomers, and the equilibrium ratio is somewhat solvent-dependent. In contrast, the *syn* isomer is the unique or very major species present in the solutions of compounds **3** to **5**, as found for **4** in the crystal. Although we have not analyzed the *syn*/*anti* isomerism in detail, it likely implies a transient cleavage of the P–MoCp bond, which allows the required rotation of the $MoCp(CO)_2$ fragment.

The phosphametallacyclopentene moieties in compounds **2** to **5** give rise to diagnostic upfield $^{31}P\{^1H\}$ NMR resonances in the range $\delta = 60$–80 ppm, which is substantially more deshielded that that in the phosphametallacyclobutene species [$Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5:\kappa^1,\eta^1\text{-}P(C_5H_4)\ CR{=}CR\}(CO)_2L$] (R = CO_2Me; $\delta_P = -24$ ppm),[7f] as expected from the different number of atoms in the metallacycle. All these resonances, however, are dramatically shielded relative to that of the phosphinidene complex **1** ($\delta_P = 519.0$ ppm).[17]

The identification of isomers and assignment of ^1H and ^{13}C NMR resonances of compounds **2** to **5** in solution was carried out using a combination of standard NOESY, DEPT, and HSQC experiments (see the Supporting Information). The acyl groups in compounds **2a,b** give rise to highly deshielded ^{13}C NMR resonances in the range $\delta = 263$–271 ppm, a position comparable to those of mononuclear molybdenum complexes with acyl ligands.[18] A medium-intensity IR band in the range 1500–1600 cm^{-1} was also observed in these compounds, which can be assigned to the corresponding C–O stretch. For compounds **3a,b**, the iminoacyl group gives rise to a less deshielded resonance at around $\delta = 206$ ppm, which is close to the values of $\delta = 220$ ppm recently reported for the related phosphametallacycles in the niobium complexes [$Nb(C_5H_4SiMe_3)_2\{\kappa^1,\eta^1\text{-}Ph_2PCR{=}CR'C(NXyl)\}$].[19]

Compounds **4** and **5** share the presence of an exocyclic NHXyl group, but with very different conformation. Thus, the N–H ^1H NMR resonance appears at $\delta = 6.40$ ppm for **4**, but at $\delta = 14.77$ ppm for **5**. This difference is interpreted as deriving from a strong intramolecular N–H···O hydrogen bonding with the ketonic oxygen in the latter case. This interaction would also facilitate some exocyclic delocalization of the double C–C bond of the metallacycle.

The formation of compounds **2** to **5** can be rationalized through the reaction pathways depicted in Scheme 3. The first step would be the addition of the carbonyl or isocyanide ligand to the $MoCp(CO)_2$ fragment to give intermediate **A** having a pyramidal phosphinidene ligand. This would greatly increase the nucleophilicity of the P atom, thus allowing it to rapidly attack the more electrophilic carbon atom of the alkyne or alkene at room temperature. Indeed, we have shown recently that the isolable diiron complex [$Fe_2Cp_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2$] with a pyramidal phosphinidene bridge is able to react with some alkynes and even CH_2CHCO_2Me at room temperature, although quite slowly in the latter case.[7e,g] Nucleophilic attack on the alkyne would lead to a zwitterionic intermediate **B** with a carbanionic center placed at the right position to attack the adjacent metal-bound CO or CNXyl ligands, thus completing the closure of the phosphametallacycle with acyl and iminoacyl functions, respectively. In the isocyanide reaction we must remark that the cyclization step takes place in a highly chemoselective way, since no acyl-type product is formed. This result suggests that the evolution of intermediate **B** might be charge-controlled, because the ligand being the less powerful π acceptor (isocyanide, rather than carbonyl in this case) is expected to bear a more positive charge at the metal-bound carbon atom.[20] In the reaction with olefins, however, the cyclization step does not lead to a stable product but to an undetected intermediate **C**, which would rapidly undergo [1,3]-H shift (comparable to the imine–enamine tautomerization), presumably favored on the "enamine" side thanks in part to the novel intramolecular



Scheme 3. Proposed reaction pathways in the formation of complexes **2**-**5**. C $\overset{D/T}{—}$ C stands for a generic alkene/alkyne molecule.

C(O)H···π and NH···O interactions that can be established in this way.

In summary, we have reported the first examples of three-component coupling reactions involving an isolable phoshinidene complex. These reactions take place rapidly at room temperature and result in a highly chemo- and regioselective coupling of the metal-bound phosphinidene, and alkene/alkyne molecule and a CO/CNXyl ligand to give with good yields dimolybdenum derivatives having novel phosphametallacyclopentene rings. Further work is now in progress to extend the above methodology to the reactions of the phosphinidene complex **1** with other dienophiles in the presence of CO, CNR, and other two-electron donor ligands.

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Keywords: cycloaddition · molybdenum · multicomponent reactions · phosphinidenes · P ligands

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[11] The Supporting Information contains the synthesis and analytical and spectroscopic data of the complexes **2**–**5**.

[12] Brown crystals of **2a**·THF were grown by slow diffusion of a layer of petroleum ether in a saturated tetrahydrofuran solution of the compound at room temperature. Green-brown crystals of **4**·CH_2Cl_2 were grown by slow diffusion of layers of diethyl ether and petroleum ether in a saturated dichloromethane solution of the compound at 253 K. CCDC 817666 and 817667 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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