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COMMUNICATION

A NOVEL DIPHOSPHORUS–MOLYBDENUM RING SYSTEM

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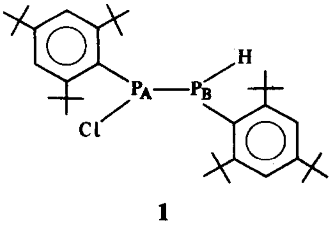
Abstract—The reaction of $ArPCl_2$ ($Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) with $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ affords Ar(H)PP(Cl)Ar (**1**), $ArP[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$ (**2**), ArP═PAr, $ArPH_2$ and Ar(H)PP(H)Ar. By means of X-ray crystallography, it was established that the Mo_2P ring of **2** involves a planar phosphorus geometry, a slight degree of Mo–P multiple bonding, and a Mo—Mo single bond. Thermolysis of the original reaction mixture produced the P_2Mo ring compound $ArPP(H)(Ar)[\mu^2\text{-}Mo(CO)_2(\eta\text{-}C_5H_5)]$ (**3**). The structure of **3** was determined by X-ray diffraction.

There are several examples of complexes of the type $R_2P\overset{\cdots}{-}ML_n$ which imply three-electron donation by phosphorus and thus a modicum of metal–phosphorus multiple bonding.[1] We describe a new type of interaction in which the $3e^-$ donation involves *two* phosphorus atoms.

A THF solution of $ArPCl_2$ ($Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) was treated with two equivalents of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ at −78°C and allowed to warm slowly to 25°C. ^{31}P NMR spectroscopic assay of the reaction mixture revealed the presence of ArP═PAr,[2] $ArPH_2$,[3] Ar(H)PP(H)Ar,[3] and two new compounds, ArP(H)PP(Cl)Ar (**1**) and $ArP[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$ (**2**). Separation of the reaction mixture by column chromatography (silica gel–*n*-hexane) resulted in the isolation of **2** (22% yield), but caused the decomposition of **1**. However, the identity of **1** as ArP(H)PP(Cl)Ar was established by the following facts: (i) the ABX ^{31}P NMR spectrum for **1** ($\delta_{P_A}+111$, $\delta_{P_B}-30$, $^1J_{P_AP_B} = 300$, $^1J_{P_BH} = 224$, $^2J_{P_AH} = 5$ Hz) is very similar to that of $(Me_3Si)_3CP(H)P(Cl)C(SiMe_3)_3$,[4] and; (ii) **1** can be produced (42% yield) (in admixture with smaller quantities of $ArPH_2$, ArP(H)PP(H)Ar and ArP═PAr) by slow addition of ArPHLi to $ArPCl_2$ in THF solution at 0°C. Compound **2** (δ_P+687) was identified as a bridging phosphinidene complex by X-ray crystallography (Fig. 1). Within experimental error, the geometry at phosphorus is trigonal planar and the Mo–P bond lengths [average 2.306(8) Å] are somewhat short and thus indicative of a slight degree of metal–phosphorus multiple bonding. The Mo–Mo bond length [3.220(8) Å], on the other hand, corresponds to a bond order of unity. The foregoing structural features for **2** are similar to those of $ArP[Co(CO)_3]_2$ (**4**).[5] While there are several



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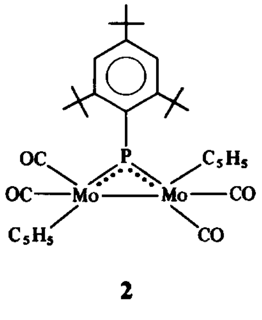

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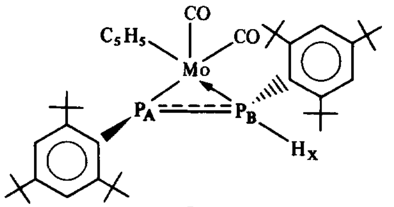
examples of complexes of the type $RP(ML_n)_2$ featuring $16e^-$ organometallic moieties,[7] the significance of **2** and **4** is that they involve $15e^-$ fragments.



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Thermolysis of the original reaction mixture (refluxing toluene, 30 min) caused the disappearance of the ^{31}P resonance due to **1** and the emergence of a new ABX pattern attributed to **3** (δ_{P_A} −151, δ_{P_B} 0.2, $^1J_{P_AP_B} = 541$ Hz, $^1J_{P_AH} = 401$ Hz, $^2J_{P_AH} < 1$ Hz). Compound **3** can also be prepared (in >90% yield) by the thermal reaction of **1** with $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$, thus suggesting its origin in the previous reaction. Purification of **3** was effected by column chromatography (silica gel–*n*-hexane) and the compound was identified by X-ray crystallography (Fig. 2) and NMR spectroscopy.[*] Hydrogen H_x was not detected in the X-ray study due to poor crystal quality; however, its presence was clear from the ABX ^{31}P NMR spectrum. Examination of the geometry around P_B indicates that H_x is pointed away from the $Mo–P_B$ bond. The simplest way to visualize the bonding in **3** is to consider it as a complex of the (as yet unprepared)[6] anion, $[ArP_A–P_B(H)(Ar)]^-$, in which P_A and P_B serve as one- and two-electron donors, respectively. The

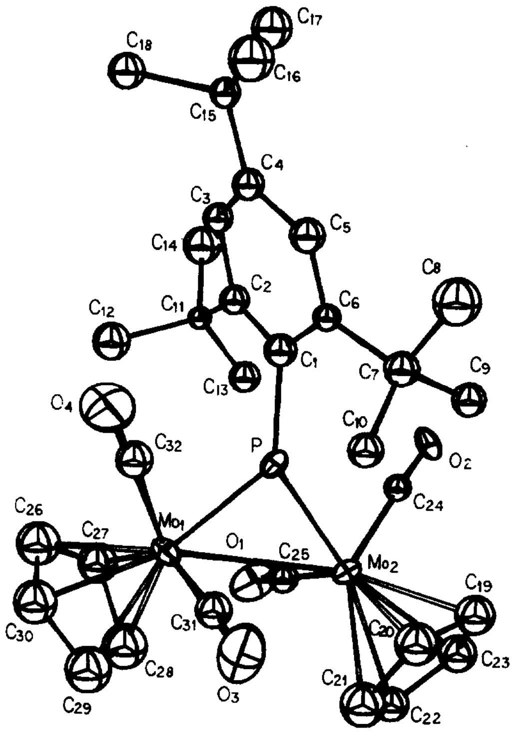

Fig. 1. ORTEP view of **2** showing the atom-numbering scheme. Important parameters: Mo(1)–Mo(2) = 3.220(8) Å, Mo(1)–P = 2.297(8) Å, Mo(2)–P = 2.315(8) Å, P–C(1) = 1.89(3) Å, Mo(1)–P–Mo(2) = 88.4(3)°.

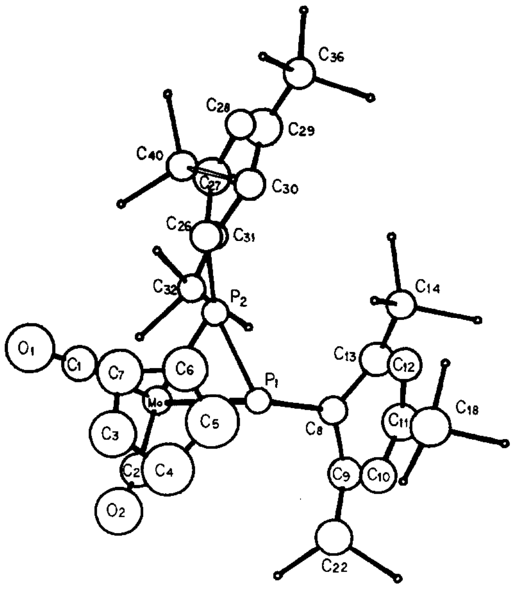

Fig. 2. ORTEP view of **3** showing the atom-numbering scheme. Important parameters: Mo–P(1) = 2.696(6) Å, Mo–P(2) = 2.389(7) Å, P(1)–P(2) = 2.145(8) Å, P(1)–Mo–P(2) = 49.4(2)°, P(2)–P(1)–Mo = 57.8(2)°, P(1)–P(2)–Mo = 72.8(3)°, P(2)–P(1)–C(8) = 103.0(8)°, P(1)–P(2)–C(26) = 124.2(7)°.

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[*] Crystal data for **2**: $C_{32}H_{39}Mo_2O_4P$; $M = 710.52$. Crystal data: monoclinic, $P2_1/c$ (No. 14); $a = 13.429(2)$ Å, $b = 13.705(2)$ Å, $c = 17.072(2)$ Å, $\beta = 97.62(1)°$; $V = 3114$ Å^3, $Z = 4$, $D_c = 1.515$ g cm^{-3}.

Crystal data for **3**: $C_{43}H_{63}MoO_2P_2$; $M = 769.87$. Crystal data: monoclinic, $P2_1/c$ (No. 14); $a = 20.456(3)$ Å, $b = 11.501(3)$ Å, $c = 18.380(6)$ Å, $\beta = 97.80(2)°$; $V = 4284$ Å^3, $Z = 4$, $D_c = 1.194$ g cm^{-3}.

Intensity data: Enraf–Nonius CAD-4F diffractometer, ω–2θ scan modes in the range $2.0 \leqslant 2\theta \leqslant 50.0°$; 3007 and 3298 unique reflections for **2** and **3**, respectively. The structure of **2** was solved by direct methods while that of **3** was solved by Patterson and difference Fourier technqiues. The structures of **2** and **3** were refined (full matrix, least squares) by using 2127 and 2940 data, respectively. Final residuals (R) were 0.0870 and 0.1030 for **2** and **3**, respectively. Atomic positional and thermal parameter coefficients, full lists of bond lengths and angles and lists of F_o/F_c values for **2** and **3** have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

P_A–Mo distance [2.389(7) Å] corresponds to a bond order of unity. The P_B–Mo bond [2.696(6) Å] is somewhat longer than normal; nevertheless, the presence of such a bonding interaction is evident from, for example, the acute Mo–P_A–P_B angle [57.8(2)°]. Interestingly, the P_A–P_B distance [2.145(8) Å] is ~0.06 Å shorter than that of a P—P single bond, suggesting a slight multiple-bond character. This results should not be over-interpreted given the mediocre quality of the crystal structure. Nevertheless, it is interesting to note that the implication of modest multiple bonding is consistent with the large ${}^1J_{P_AP_B}$ coupling constant.[8]

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