

An uncommon bonding mode of a familiar ligand: a molybdenum complex with a four-electron donor chelating η^3 -PPh₃ ligand, and its structural determination using synchrotron radiation

Tan-Yun Cheng, David J. Szalda† and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA.

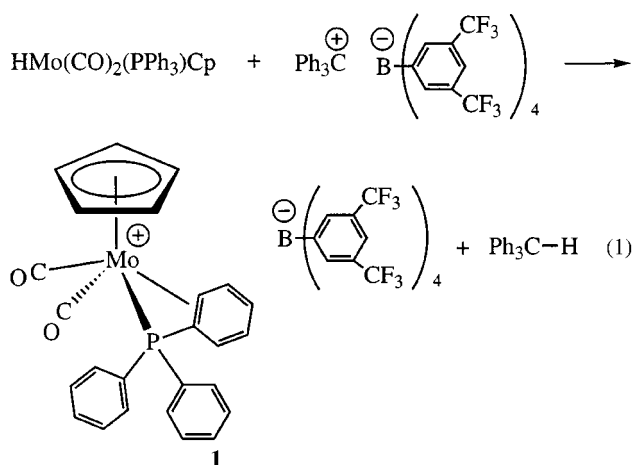
E-mail: bullock@bnl.gov

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A crystallographic study using synchrotron radiation shows that a C=C bond of one phenyl group of a PPh₃ ligand bonds to Mo in [Cp(CO)₂(PPh₃)Mo]⁺, resulting in an unusual bonding mode in which PPh₃ functions as a chelating four-electron donor ligand.

The triphenylphosphine ligand occupies a prominent role in organometallic chemistry and homogeneous catalysis. The traditional mode of bonding of PPh₃ is as a two-electron donor through the lone pair on the phosphorus atom. We have prepared a new complex in which PPh₃ functions as a chelating four-electron donor ligand, with a C=C bond of one phenyl group bonding to the metal. A structural determination by X-ray crystallography was carried out using synchrotron radiation. Weak C-F...H-C interactions are found between C-F groups on the BAR'₄[−] [Ar' = 3,5-bis(trifluoromethyl)phenyl] counterion and ligand C-H groups on the cationic molybdenum complex.

Hydride transfer from Cp(CO)₂(PPh₃)MoH to Ph₃C⁺BF₄[−] gives Cp(CO)₂(PPh₃)MoF₃.¹ In this reaction and many others reported by Beck and co-workers, the 16-electron metal cation resulting from removal of hydride is captured by a weakly coordinating counterion such as BF₄[−].² We recently measured the kinetics of this and several related hydride transfer reactions using stopped-flow techniques.³ We have found that a completely different product results when hydride abstraction from Cp(CO)₂(PPh₃)MoH is carried out using a counterion that is much more weakly coordinating than BF₄[−]. Reaction of Ph₃C⁺BAR'₄[−] with Cp(CO)₂(PPh₃)MoH at −30°C led to the isolation of a new complex (**1**) in 84% yield [eqn. (1)].⁴



The ¹³C NMR spectrum of **1** at −60 °C exhibits a doublet (*J*_{CP} = 29 Hz) at δ 81.5 and another doublet (*J*_{CP} = 12 Hz) at

δ 90.0. These resonances are assigned as the *ipso* and *ortho* carbons of one of the C=C bonds of the Ph ring. The significant upfield shift of these carbons from the other aromatic carbons (δ 120–135) suggests that one C=C bond of the ring is coordinated to the molybdenum, as indicated in eqn. (1).

Remarkable progress has been made recently in the design and utility of large, weakly coordinating counterions.⁵ A serious drawback often encountered is the difficulty of obtaining single crystals that are large enough and that diffract well. Initial attempts to obtain a crystal structure of **1** using a conventional X-ray diffractometer suffered from an insufficient number of observed data to enable a complete refinement. The use of a high intensity source of X-rays, such as a synchrotron, can provide sufficient scattering to obtain a reliable structural determination. The crystal structure of **1** was successfully solved and refined⁶ using data collected from a beamline at the National Synchrotron Light Source at Brookhaven. A significant advantage of using a synchrotron source of X-rays is that small crystals are suitable; the crystal we used had dimensions of 0.02 × 0.08 × 0.08 mm. The use of synchrotron radiation may offer advantages for single crystal diffraction studies of other complexes of large, weakly coordinating counterions, as well as other complexes for which only small crystals suitable for diffraction can be obtained.

The ORTEP diagram in Fig. 1 shows that the Mo is located out of the plane of the arene ring. The distortion of the PPh₃ ligand is evidenced by the acute Mo–P–C(31) angle of 73.0(3)°, compared to angles of 117.8(3)° and 131.3(4)° for the other two Mo–P–C bonds. The dihedral angle between the Mo–C–C plane and the plane of the phenyl ring is 62°. The bond distances of the Ph ring bonded to Mo show some evidence of localization of C=C and C–C bonds. Similar structural parameters were found

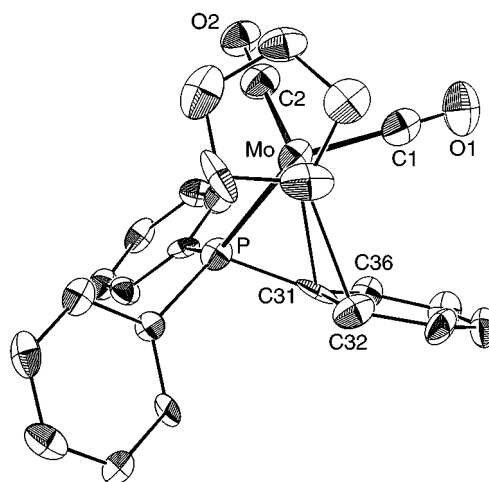


Fig. 1 ORTEP diagram of **1** showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Mo–C(2) 1.968(12); Mo–C(1) 1.99(2); Mo–P 2.429(3); Mo–C(31) 2.566(9); Mo–C(32) 2.645(9); C(31)–C(32) 1.418(13); C(31)–C(36) 1.445(14); C(32)–C(33) 1.424(14); C(33)–C(34) 1.361(14); C(34)–C(35) 1.404(13); C(35)–C(36) 1.368(13); C(2)–Mo–C(1) 79.7(5); C(2)–Mo–P 83.8(3); C(1)–Mo–P 115.7(3).

† Research Collaborator at Brookhaven National Laboratory. Permanent Address: Department of Natural Sciences, Baruch College, New York, NY 10010, USA.

in other $M(\eta^2\text{-arene})$ complexes, such as $\text{Cp}^*(\text{PMe}_3)\text{Rh}(\eta^2\text{-phenanthrene})$,⁷ $\text{Cp}^*(\text{NO})\text{Ru}(\eta^2\text{-naphthalene})$,⁸ and $[(\text{NH}_3)_5\text{Os}(\eta^2\text{-naphthalene})]^{2+}$.⁹ An $\eta^2\text{-C}=\text{C}$ bond of a *p*-tolyl group was shown to be bound to tungsten in a series of bimetallic compounds where the *p*-tolyl group was part of a bridging alkylidene in a $W[\mu\text{-C}(p\text{-tolyl})(\text{R})]\text{Pd}$ moiety.¹⁰

In several previously reported examples where a metal bonds to the phenyl group of a PPhR_2 ligand, the CH bond of the arene interacts with the metal in an $\eta^2\text{-CH}$ agostic¹¹ interaction, rather than the $\eta^2\text{-C}=\text{C}$ bonding found here. Structurally characterized phosphine complexes with agostic C–H interactions include $\text{Pd}(\text{PPh}^t\text{Bu}_2)_2$,¹² $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$,¹³ $\text{RuCl}_2(\text{PPh}_3)_3$,¹⁴ and $\text{PdI}_2(\text{PPhMe}_2)_2$.¹⁵ These $\eta^2\text{-CH}$ agostic complexes have conspicuous structural differences that contrast with $\eta^2\text{-arene}$ complexes: the metal is normally nearly coplanar with the arene ring (dihedral angle of $< 15^\circ$ between M–C–C and arene planes) and the M–P–C angles are typically $111\text{--}114^\circ$ rather than the acute Mo–P–C(31) angle of $73.0(3)^\circ$ noted above. Although it has been suggested¹¹ that $[\text{Rh}(\text{PPh}_3)_3]^+$ ¹⁶ has an agostic interaction, its structural features (Rh–P–C angle of $75.6(5)^\circ$; dihedral angle of 59° between Rh–C–C and arene planes) are much more similar to those found in **1**. Accordingly, we suggest that $[\text{Rh}(\text{PPh}_3)_3]^+$ ¹⁶ has an $\eta^2\text{-arene}$ interaction, rather than agostic, and we believe that these structural criteria will be diagnostic in distinguishing between agostic and $\eta^2\text{-arene}$ interactions in other complexes. Other than complex **1** reported here and $[\text{Rh}(\text{PPh}_3)_3]^+$ which we interpret as having an $\eta^2\text{-CH}$ arene interaction, we are not aware of other examples where a PPh_3 ligand bonds to a metal as a four-electron donor in an $\eta^3\text{-bonding}$ mode. There are, however, examples of $\eta^2\text{-C}=\text{C}$ bonds in Ru complexes with chelating diphosphine ligands BINAP¹⁷ or MeO-BIPHEP.¹⁸ These diphosphines are bridged by substituted-biphenyl groups.

The structural determination of **1** reveals a series of weak C–F...H–C interactions, with over twenty F...H distances in the range of $2.6\text{--}3.0\text{ \AA}$. The presence of F...H–C interactions¹⁹ has been observed in a variety of compounds recently,²⁰ though their assignment as hydrogen bonds is not without controversy.²¹

Although **1** was isolated as a pure solid, it decomposes slowly at room temperature (several days in CD_2Cl_2 solution or a few months as a solid). The weak $\text{C}=\text{C}$ bond of **1** is readily and cleanly displaced by ligands such as CH_3I and H_2O . Further spectroscopic and structural studies of these compounds will be reported.

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