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Terminal chloroaminophosphido and aminophosphinidene complexes of molybdenum

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Abstract

The phosphido complex [$Cp^*Mo(CO)_3P(Cl)N^iPr_2$] (**1**, $Cp^* = C_5(CH_3)_5$) was formed by the reaction of Li[$Cp^*Mo(CO)_3$] with $^iPr_2NPCl_2$. Chloride abstraction from **1** leads to the aminophosphinidene complex [$Cp^*(CO)_3Mo{=}PN^iPr_2$][$AlCl_4$] (**2**) which reacts with phenylacetylene to form the metalaphosphacyclobutene complex [$Cp^*(CO)_3\overline{Mo\{P(N^iPr_2)C(Ph){=}C}H\}$][$AlCl_4$] (**3**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphinidene; Aminophosphinidene; Phosphido; Chloroaminophosphido; Molybdenum

1. Introduction

Although terminal phosphinidene complexes are receiving an increasing amount of attention, well characterized examples remain relatively rare [1]. The first examples of terminal phosphinidene complexes described by Lappert were $Cp_2M{=}PR$ ($M = Mo$, $R = 2,4,6\text{-}^tBu_3C_6H_2$; $M = W$, $R = 2,4,6\text{-}^tBu_3C_6H_2$, $(Me_3Si)_2CH$) [2]. Since then, phosphinidene complexes of Zr [3], Ta [4], and U [5], including examples with formal metal–phosphorus triple bonds, have been described. Most of these examples are formally derived from a free phosphinidene with a triplet ground state and are thus analogous to Schrock type carbenes. Introduction of π-donor substituents onto phosphorus, however, should stabilize the singlet state of the free phosphinidene and result in complexes analogous to Fischer carbenes. Phosphinidenes of this type have proven to be more elusive. A base-stabilized example of an aminophosphinidene complex of iron has been described [6], and spectroscopic evidence for transient aminophosphinidenes has been reported [7].

Transient phosphinidene complexes, including aminophosphinidenes have proven useful in the synthesis of organophosphorus compounds. In particular, [$(CO)_5WPPh$], generated in situ by the decomposition of phosphanorbornadiene complexes reacts with imines [8], alkenes [9], dienes [10], alkynes [11], diynes [12], and chloroalkenes [13] to form a variety of products. Similarly, $^iPr_2NP{=}Fe(CO)_4$, generated in situ by the reaction of $[Fe(CO)_4]^{2-}$ with $^iPr_2NPCl_2$, reacts with allenes [14] and alkynes [15] to form phosphiranes and phosphirenes.

This paper reports the synthesis of a chloroaminophosphido complex of molybdenum and chloride extraction to form an aminophosphinidene complex which has been characterized spectroscopically and by the product of its reaction with phenylacetylene.

2. Results and discussion

2.1. Synthesis of the terminal phosphido complex [$Cp^*Mo(CO)_3P(Cl)N^iPr_2$] (1)

Compound **1** is readily prepared by the reaction of the $Cp^*Mo(CO)_3^-$ anion with $^iPr_2NPCl_2$. Unexpectedly, in the major product only one chloride is displaced from the phosphine even if an excess of the molybdenum anion is used. This reactivity is attributed to the steric size of the Cp* ligand since in related systems with cyclopentadienyl ligands [16], the reaction proceeds to the μ_2 phosphinidene via displacement of both chlorides.

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The infrared spectrum of compound **1** contains three strong, sharp carbonyl stretches at 2008, 1941, 1923 cm^{-1}, clearly indicating that the molybdenum center retains three carbonyl ligands. The resulting electron count then indicates that the phosphido ligand must be acting as a net one-electron donor, as opposed to a three electron donor phosphido ligand in which the lone pair on phosphorus is donated to the metal. Compound **1** can thus be described as a metallo-phosphine. The tricarbonyl phosphido complex contrasts with the only other published example of a molybdenum chloroamino phosphido complex, namely CpMo(CO)$_2$P(Cl)-tmp (tmp = 2,2,5,5-tetramethylpiperidenyl). In this complex the phosphido ligand acts as a three electron donor [13b]. The reactivity difference is likely attributable to the less basic Cp ligand, as well as the greater steric bulk of the tmp group on the phosphorus.

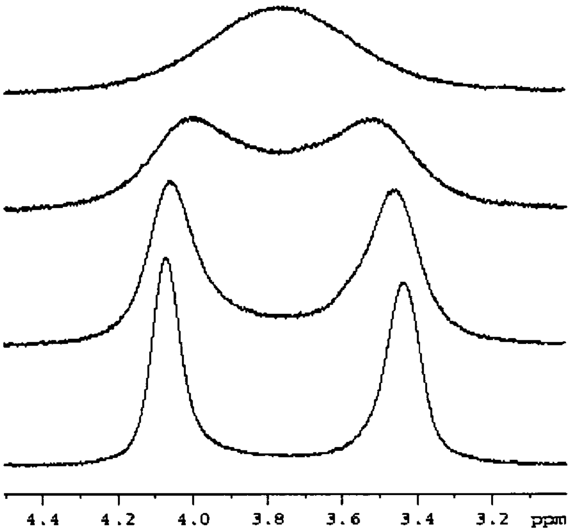


Fig. 1. Variable temperature ^{1}H-NMR spectrum of [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)] (**1**), showing the coalescence of the isopropyl methyne hydrogen atoms. Temperatures shown are 35, 45, 55 and 65°C.

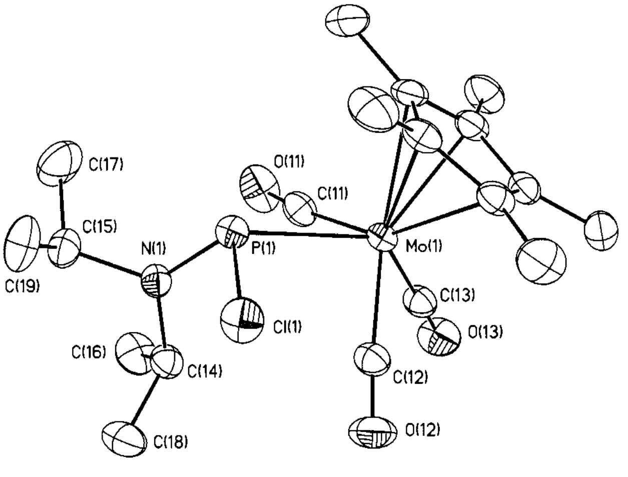


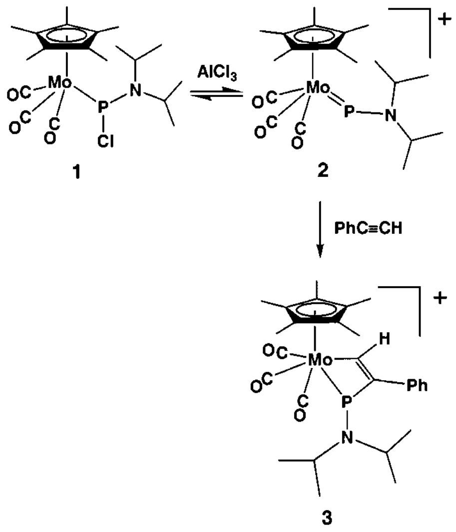
Fig. 2. Structural diagram of [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)]. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been eliminated for clarity.

The ^{31}P{^{1}H}-NMR spectrum of compound **1** displays a singlet at δ 313.7, while the ^{1}H-NMR spectrum shows broad resonances for two inequivalent isopropyl groups and four methyl groups. Below 0°C, the CH resonances resolve into septets, while the methyl groups give rise to four doublets suggesting that there is an exchange process occurring. EXCY spectroscopy was used to show that the two isopropyl CH groups are exchanging and all four methyl groups are exchanging. If we assume facile inversion at nitrogen, based upon the near planarity of this atom in the solid state (vide infra), the inequivalence of the isopropyl groups must result from a barrier to rotation about the P–N single bond which could result from interaction of the lone pairs on each of these atoms, or from classical π donation from nitrogen to phosphorus [17]. The appearance of four methyl groups indicates that there is also a barrier to inversion at phosphorus that results in a stereogenic center and diastereotopic methyl groups. Coalescence of the CH resonances occurs at 61°C (see Fig. 1), allowing an estimate of 15.4 ± 0.4 kcal mol^{-1} for the barrier to rotation about the PN bond. This process also results in coalescence of four methyl resonances into two. The coalescence temperature for the second process was not reached at 80°C but we can estimate a lower limit of 17 kcal mol^{-1} for the barrier to inversion at phosphorus. Reported barriers to inversion at phosphorus in metal phosphido complexes range from 11.5 to 18.0 kcal mol^{-1} [18].

Compound **1** has been characterized by X-ray crystallography and is the first structurally characterized example of a one-electron donor chloroaminophosphido complex. An ORTEP diagram of the molecule is shown in Fig. 2 and selected bond lengths and angles are given in Table 1. The geometry at Mo is that of a square based pyramid with three carbonyls and the phosphido ligand forming the base and the Cp* ligand in the apical position. All parameters involving the carbonyl and Cp* ligands are as expected. The Mo–P bond distance of 2.5646 (7) Å is in the normal range for a Mo–P single bond [19]. In addition to the Mo, the phosphorus atom is bound to chlorine (P–Cl = 2.205 (1) Å) and nitrogen. The P–N distance (1.672 (2) Å) falls in the middle of the normal range for a P–N single bond suggesting that there is no multiple P–N bonding. The geometry at phosphorus is clearly pyramidal; the phosphorus position deviates from the plane formed by Mo, Cl and N by 0.744(1) Å. In contrast, the nitrogen is nearly planar, with a deviation from the P(1)–C(14)–C(15) plane of only 0.124(2) Å. The nitrogen substituents are staggered with respect to those on the phosphorus atom.

Table 1
Selected bond lengths (Å) and angles (°) for [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)] (**1**)

Bond lengths			
Mo–C(13)	1.987(3)	O(11)–C(11)	1.151(4)
Mo–C(11)	1.993(3)	O(12)–C(12)	1.140(4)
Mo–C(12)	1.999(3)	O(13)–C(13)	1.145(4)
Mo–P	2.5646(7)	C(14)–C(16)	1.523(4)
Cl–P	2.2053(10)	C(14)–C(18)	1.528(5)
P–N	1.673(2)	C(15)–C(17)	1.516(5)
N–C(14)	1.480(4)	C(15)–C(19)	1.524(5)
N–C(15)	1.491(4)		
Bond angles			
C(13)–Mo–C(11)	78.62(13)	C(15)–N–P	116.56(19)
C(13)–Mo–C(12)	77.16(12)	O(11)–C(11)–Mo	174.3(3)
C(11)–Mo–C(12)	113.50(12)	O(12)–C(12)–Mo	175.1(3)
C(13)–Mo–P	132.11(9)	O(13)–C(13)–Mo	178.2(3)
C(11)–Mo–P	74.36(9)	N–C(14)–C(16)	111.7(3)
C(12)–Mo–P	78.45(9)	N–C(14)–C(18)	112.2(3)
N–P–Cl(1)	104.02(9)	C(16)–C(14)–C(18)	111.3(3)
N–P–Mo	114.18(9)	N–C(15)–C(17)	110.2(3)
Cl–P–Mo	105.01(3)	N–C(15)–C(19)	113.2(3)
C(14)–N–C(15)	115.6(2)	C(17)–C(15)–C(19)	111.6(3)
C(14)–N–P	125.89(19)		



Scheme 1.

2.2. Chloride abstraction

The chloride ligand on the chloroaminophosphido ligand can be readily abstracted using the Lewis acid aluminium chloride resulting in the formation of the aminophosphinidene complex [Cp*Mo(CO)$_3$(=PN^{i}Pr$_2$)][AlCl$_4$] (**2**), as shown in Scheme 1. Compound **2** is deep red in color and forms extremely air and water sensitive solutions. The ^{31}P-NMR spectrum of **2** shows an extremely low-field resonance at δ 1007.5 which is characteristic of most phosphinidene complexes [1–7]. To date, this is the highest chemical shift observed for a terminal phosphinidene complex. The IR spectrum shows three carbonyl stretching bands at 2041, 1986, and 1959 cm^{-1}. The IR frequencies are significantly higher than those of the Mo(II) phosphido complex **1** and are very similar to those of the heterocyclic Mo(IV) complex **3** (vide infra) suggesting that **2** is best formulated as a complex of Mo(IV).

The ^{1}H-NMR spectrum of **2** shows two inequivalent isopropyl groups. Unlike in the starting phosphido complex, the methyl groups are not diastereotopic since the phosphorus is no longer stereogenic, but there remains a barrier to rotation about the P–N bond, which renders the isopropyl groups inequivalent. In this case, there is no evidence of exchange between the two isopropyl groups. One of the CH resonances shows a coupling constant of 5.9 Hz to phosphorus, while the other shows no P coupling. These results indicate that there is no rotation about the PN bond and suggest that the PNC$_2$ unit is planar and that there is multiple bonding between phosphorus and nitrogen. Density functional studies of transition metal phosphinidene complexes by Ehlers et al. [20] and Creve et al. [21] suggest that π donation from the substituent on phosphorus plays an important role and competes with back donation from the transition metal. The observed restricted rotation about the PN bond in **2** provides experimental support for this theoretical prediction.

Although previous examples have been identified by phosphorus chemical shift and subsequent reaction products [4], this is the first aminophosphinidene that has been well characterized spectroscopically.

The reaction of phosphido complex **1** with AlCl$_3$ is rapid and reversible, although the equilibrium lies toward compound **2**. At room temperature, a mixture of **1** and **2**, formed by the addition of half an equivalent of AlCl$_3$ to **1**, exchanges rapidly such that the observed ^{31}P spectrum contains one broad signal that is the average of the resonances of **1** and **2**. At -90°C, the resonance broadens into the baseline but decoalescence could not be achieved. The rapid equilibrium suggests the possibility that the AlCl$_4^-$ counterion in **2** remains closely associated with the complex. Attempts to isolate **2** as a solid or to exchange the counterion resulted in rapid decomposition.

2.3. Reaction of the phosphinidene complex with phenyl acetylene

Phosphinidene complexes of transition metals have been shown to be useful reagents in the synthesis of organophosphorus compounds. In order to provide further confirmation of the nature of **2** and demonstrate the reactivity of the phosphinidene complex, its behavior towards phenylacetylene was examined. As shown in Scheme 1, the reaction results in a $2+2$ cycloaddition to form the phosphametalocyclobutene product **3**. Alkyne addition is regiospecific, with only one isomer observed in which the phenyl group is on the carbon adjacent to phosphorus and is directed away from the metal center.

Compound **3** has been isolated and fully characterized by spectroscopy and microanalysis. The IR spectrum shows three bands at 2045, 1977, and 1960 which exhibit a shift to higher frequency compared to those of the phosphido complex **1**, as would be expected in moving from Mo(II) to Mo(IV). However, the IR bands are very similar to those of the phosphinidene complex **2**. The ^{31}P chemical shift of **3** is δ -75.5, strikingly different from the $+313$ shift of compound **1**, although **3** is also an aminophosphinidene. The shift to lower frequency is attributed to the fact that the phosphorus atom is part of a four membered ring [22].

In the ^{1}H-NMR spectrum, the olefinic hydrogen appears as a doublet at δ 9.06 with a *trans* coupling to phosphorus of 17 Hz. The corresponding olefinic carbon appears at δ 130.18 and shows a small phosphorus coupling of 4 Hz, leading to its assignment as the Mo bound carbon, rather than the P-bound carbon. The correlation between this carbon and the olefinic hydrogen was confirmed with an HMQC experiment. The small coupling between this olefinic carbon and phosphorus suggests that compound **3** is not a phosphirene, and although we can not completely rule out this possibility, we favor the structure shown. The phenyl substituted olefinic carbon appears at δ 161.4 as a doublet with phosphorus coupling of 30.5 Hz. The *ipso* carbon of the phenyl group also shows a small phosphorus coupling, providing supporting evidence that the phenyl substituted olefinic carbon is the one bound to phosphorus.

The isopropyl groups in **3** are equivalent, with the methyne proton giving rise to a doublet of septets at δ 3.47 with coupling to phosphorus as well as to the methyl groups. The methyl groups are diastereotopic due to the stereogenic phosphorus center, appearing as doublets at δ 1.22 and 1.13. It is not clear why there is free rotation about the PN bond in **3** while the rotation is restricted in **1**.

The reactivity of the phosphinidene complex **2** with phenylacetylene parallels that of the zirconium phosphinidene complex $[Cp_2Zr(=PR)PMe_3]$ ($R = C_6H_2$-2,4,6-$^{t}Bu_3$) [23], but contrasts with the reactivity of transient phosphinidenes such as $(CO)_5M{=}PPh$ (M = Cr, Mo, W) [8] and $(CO)_4Fe{=}PN^{i}Pr_2$ [12], which react with alkynes to form phosphirene rings. Mathey et al. [24] have suggested two classes of phosphinidenes, nucleophillic and electrophillic, paralleling Schrock and Fischer type carbenes. The reactivity of **2** with phenylacetylene suggests that it can be classified as a nucleophillic phosphinidene despite the presence of the amine substituent. We have considered the possibility that the initial product of the reaction with phenylacetylene is the phosphirene and that subsequent oxidative addition leads to compound **3**, however low temperature reactions failed to reveal any intermediate species. Further reactivity studies with other unsaturated organic substrates are underway to clarify the nature of the phosphinidene complex.

Because it is easily synthesized in high yield from inexpensive starting materials, the phosphinidene complex **2** has great potential as a synthetic reagent for organophosphorus chemistry.

3. Experimental

3.1. General comments

All procedures were carried out using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. Hexane and THF were distilled from Na–benzophenone. Dichloromethane was distilled over CaH_2 and further purified by vacuum distillation from P_2O_5. Deuterated $CHCl_3$ was distilled from P_2O_5, while CD_2Cl_2 and toluene-d_8 were purchased from CIL in ampules and used as received. The NMR spectra were recorded on a Bruker Avance 400 spectrometer using $CDCl_3$ solvent, except for low and high temperature studies, which were carried out in CD_2Cl_2 and toluene-d_8, respectively. The compound $^{i}Pr_2NPCl_2$ was synthesized using the literature procedure [25].

3.2. $[Cp^*Mo(CO)_3P(Cl)N^iPr_2]$ (1)

To pentamethylcyclopentadiene (0.52 g, 3.8 mmol, 0.60 ml) in 50 ml of THF was added *n*-butyl lithium (1.5 ml of 2.5 M solution in hexane). Molybdenum hexacarbonyl (1.00 g, 3.78 mmol) was then added and the resulting suspension was heated under reflux for 12 h resulting in a yellow solution of $Li[Cp^*Mo(CO)_3]$. This solution was added in small portions over 2 h to a solution of $^{i}Pr_2NPCl_2$ (1.0 ml, 6.7 mmol) in 75 ml of THF resulting in a yellow–orange solution. The solvent was removed in vacuo and the residue was extracted into 25 ml of hexane and filtered to remove LiCl. The yellow hexane solution was then cooled to −25°C for 24 h resulting in the formation of large, yellow crystals, which were collected by filtration. The volume of the supernatant was then reduced and the crystallization step was repeated. Overall yield from four successive crystallizations is 1.273 g (70%). Anal. Calc. for $C_{19}H_{29}ClMoNO_3P$: C, 47.36; H, 6.06; N, 2.91. Found:

C, 47.67; H, 5.82; N, 2.87%. IR νCO (hexane): 2008ss, 1941ss, 1923ss. ^{1}H-NMR (25°C): δ 3.87 (b, 1H, C*H*(CH$_3$)$_2$), 3.62 (b, 1H, C*H*(CH$_3$)$_2$), 1.96 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.51 (b, 3H, C*H*$_3$), 1.28 (b, 3H, C*H*$_3$), 1.17 (b, 6H, C*H*$_3$). ^{1}H-NMR (−30°C, CD$_2$Cl$_2$): δ 3.84 (septet, 1H, $^3J_{HH} = 6.6$, C*H*(CH$_3$)$_2$), 3.62 (septet, 1H, $^3J_{HH} = 6.8$, C*H*(CH$_3$)$_2$), 1.96 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.50 (d, 3H, $^3J_{HH} = 6.8$, C*H*$_3$), 1.24 (d, 3H, $^3J_{HH} = 6.6$, C*H*$_3$), 1.15 (d, 3H, $^3J_{HH} = 6.8$, C*H*$_3$), 1.13 (d, 3H, $^3J_{HH} = 6.6$, C*H*$_3$). ^{31}P-NMR: δ 313.7. ^{13}C-NMR: δ 238.0 (d, $^2J_{PC} = 9$ Hz, *C*O), 229.5 (d, $^2J_{PC} = 8$ Hz, *C*O), 225.5 (s, *C*O).

3.3. [Cp*Mo(CO)$_3$(=PN^{i}Pr$_2$)][AlCl$_4$] (**2**)

The compounds [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)] (**1**) (36 mg, 0.075 mmol) and AlCl$_3$ (10 mg, 0.075 mmol) were dissolved in 0.6 ml of CDCl$_3$ resulting in a rapid color change from yellow to deep red. The ^{1}H- and ^{31}P-NMR spectra were recorded immediately, and re-recorded after 12 h. Compound **2** is stable in solution with some decomposition over this time period, but is very air and water sensitive. Attempts to isolate **2** as a solid resulted in decomposition. IR νCO (CH$_2$Cl$_2$): 2041s, 1986s, 1959s. ^{1}H-NMR: δ 5.11 (septet, 1H, $^3J_{HH} = 6.6$, C*H*(CH$_3$)$_2$), 4.96 (doublet of septets, 1H, $^3J_{HH} = 6.7$, $^3J_{HP} = 5.9$, C*H*(CH$_3$)$_2$), 2.24 (singlet, 15H, C$_5$(C*H*$_3$)$_5$), 1.64 (doublet, 6H, $^3J_{HH} = 6.6$, C*H*$_3$), 1.50 (doublet, 6H, $^3J_{HH} = 6.7$, C*H*$_3$), ^{31}P-NMR: δ 1007.5.

Table 2
Crystal data and structure refinement for [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)] (**1**)

Empirical formula	$C_{19}H_{29}ClMoNO_3P$
Formula weight	481.79
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.4788(4)
b (Å)	9.0871(4)
c (Å)	15.1188(7)
α (°)	102.4150(10)
β (°)	98.4770(10)
γ (°)	96.8280(10)
V (Å^3)	1111.44(9)
Z	2
D_{calc} (mg m^{-3})	1.440
Absorption coefficient (mm^{-1})	0.799
F(000)	496
θ range for data collection (°)	1.40–28.73
Limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$
Reflections collected	13 211
Unique	5692 [$R_{int} = 0.0227$]
Completeness to θ	28.73 (98.8%)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5692/0/235
Goodness-of-fit on F^2	1.029
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0422$, $wR_2 = 0.1097$
R indices (all data)	$R_1 = 0.0455$, $wR_2 = 0.1125$
Largest difference peak and hole (e Å^{-3})	4.425 and −0.866

3.4. [Cp*(CO)$_3$Mo(P(N^{i}Pr$_2$)C(Ph)=C(H))][AlCl$_4$]·CH$_2$Cl$_2$ (**3**)

The compound [Cp*Mo(CO)$_3$(P(Cl)N^{i}Pr$_2$)] (**1**) (70 mg, 0.145 mmol) and aluminium trichloride (19 mg, 0.15 mmol) were dissolved in 2 ml of CH$_2$Cl$_2$ resulting in the formation of a deep red solution. Phenylacetylene (22 mg, 24 μl, 0.22 mmol) was then added resulting in an immediate color change to yellow. Hexane (30 ml) was added rapidly to the solution resulting in the formation of an oil which solidified to a fine yellow powder with stirring. The solid was collected by filtration, washed with 3 × 10 ml of hexane, and dried in vacuo. Yield: 60 mg, 57%. Anal. Calc. for C$_{28}$H$_{37}$AlCl$_6$MoNO$_3$P: C, 41.92; H, 4.60; N, 1.70. Found: C, 42.04; H, 5.40; N, 2.50%. ^{1}H-NMR confirmed the presence of co-crystallized CH$_2$Cl$_2$. IR ν(CO): 2045ss, 1977sb, 1960sh, ^{1}H-NMR: δ 9.06 (d, 1H, $^3J_{HP} = 17$, C*H*), 7.8, 7.6, 7.4 (C$_6$*H*$_5$), 3.47 (doublet of septets, 2H, $^3J_{HH} = 6.9$, $^3J_{HP} = 18$, C*H*(CH$_3$)$_2$), 1.95 (singlet, 15H, C$_5$(C*H*$_3$)$_5$), 1.22 (doublet, 6H, $^3J_{HH} = 6.8$, C*H*$_3$), 1.13 (doublet, 6H, $^3J_{HH} = 6.8$, C*H*$_3$). ^{31}P{^{1}H}: δ −74.8. ^{31}P: −74.8 (doublet of triplets, ^3J(PH$_2$) = 18, ^3J(PH) = 17). ^{13}C-NMR: δ 231.4 (d, $^2J_{PC} = 45$, *C*O), 230.4 (d, $^2J_{PC} = 1.4$, *C*O), 227.5 (d, $^2J_{PC} = 41$, *C*O), 161.4 (d, $^1J_{PC} = 30.5$, *C*Ph), 133.12 (*C*$_6$H$_5$), 130.31 (*C*$_6$H$_5$), 130.18 (d, $^2J_{PC} = 4$, *C*H), 129.3 (*C*$_6$H$_5$), 125.97 (d, $^2J_{PC} = 3.3$, *ipso* *C*$_6$H$_5$), 109.38 (*C*$_5$(CH$_3$)$_5$), 49.20 (d, $^2J_{PC} = 4.2$, *C*H(CH$_3$)$_2$), 23.45 (d, $^3J_{PC} = 4.3$, *C*H$_3$), 23.30 (d, $^3J_{PC} = 2.8$, *C*H$_3$).

3.5. Crystallographic analyses

A yellow–orange crystal of **1** was mounted on a glass fiber. Diffraction measurements were made on a Siemens SMART CCD automatic diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. The unit cell was determined from randomly selected reflections obtained using the SMART CCD automatic search, center, index and least-squares routines. Crystal data and collection parameters are listed in Table 2. Integration was carried out using the program SAINT and an absorption correction was performed using SADABS. Structure solution was carried out using the SHELXTL 5.1 suite of programs. The space group $P\bar{1}$ was chosen based on the $E^2 - 1$ value and confirmed by successful solution. The initial solution was obtained by direct methods and refined by successive least-squares cycles. In the final electron density map, the largest residual peak of 4.42 e Å^{-3} was associated with the Mo atom.

4. Supplementary information

The crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center CCDC No. 149972. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Tables of structure factors are available from the authors upon request.

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