Some P–H bond substitution derivatives and fluxionality of Cp₂Mo₂(μ-H)(μ-PHPh)(CO)₄

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Abstract

Reaction of PH₂Ph with Cp₂Mo₂(CO)₄ (Mo=Mo) results in sequential formation of Cp₂Mo₂(CO)₄(PH₂Ph)₂ and fluxional Cp₂Mo₂(μ-HXμ-PHPh)(CO)₄. Proton abstraction from Cp₂Mo₂(μ-HXμ-PHPh)(CO)₄ affords [Cp₂Mo₂(μ-PHPh)(CO)₄]⁻ while reaction with [Ph₂CIPF₆] yields fluxional Cp₂Mo₂(μ-HXμ-PFPh)(CO)₄.

Introduction

The use of clusters supported on refractory oxides for the purpose of preparing specific surface ensembles for catalysis continues to attract attention [1–3]. Use of heteroatom clusters has been suggested as a means of inhibiting cluster fragmentation via reactions with the surface [4,5]. We have reported the preparation of several sulfido bimetallic clusters [6] and their use as supported catalyst precursors and models [7,8]. We sought to prepare an analogous series of phosphinidene clusters [8] using Cp₂Mo₂(CO)₄(μ-PHPh)(μ-H) (1) as a cluster synthon. Although 1 proved to be a poor synthon for clusters containing the Mo₂PPh group, we found several aspects of the fluxional behavior and reactivity of 1 that merited reporting.

Results and discussion

Complex 1 has been prepared previously by the reaction of PhPH₂ with Cp₂Mo₂(CO)₆ (2) at 90°C in toluene [9]. Since 2 is converted to Cp₂Mo₂(CO)₄⁻(Mo=Mo) (3) under these conditions [10], we allowed PhPH₂ to react directly with
3 at room temperature. Under these conditions, the intermediate bis(phosphine) adduct 4 (eq. 1) precipitates from solution and may be recovered in 69% yield.

$$\text{Cp}_2\text{Mo}_2(\text{CO})_4 + 2\text{L} \rightarrow \text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}_2 \rightarrow \text{Cp}_2\text{Mo}_2(\mu-\text{H})(\mu-\text{PHPh})(\text{CO})_4 \quad (4)$$

In the IR spectrum of 4, the $\nu(\text{CO})$ bands appear at the relatively low frequencies of 1862 sh and 1844 cm$^{-1}$. Such low frequencies suggest that the steric bulk of the two phosphine ligands forces the carbonyl groups into semi-bridging positions. The appearance of one peak each for the Cp and PH$_2$Ph protons in the $^1$H NMR spectrum and only one signal for the carbonyl carbons in the $^{13}$C NMR indicates that 4 is fluxional at room temperature and has apparent $C_{2v}$ symmetry on the NMR time scale. The low solubility and consequent poor signal to noise ratio made a detailed line shape analysis impractical.

The reaction of triply bonded 3 with PhPH$_2$ is similar to the reactions of 3 with PPh$_3$ [10] and with PH$_3$ or MePH$_2$ [11]. In the former reaction, the bis(phosphine) adduct is isolated, but with the latter phosphines, the bis(adducts) were detected as intermediates in the formation of $\mu$-phosphide complexes.

Prolonged stirring of toluene suspensions of 4 resulted in the expected hydride 1. This reaction was conveniently followed by $^1$H NMR spectroscopy. Freshly prepared CDCl$_3$ samples of 4 showed a single, phosphorus-coupled Cp resonance [â 4.83 (d, 10H, $J(\text{PH}) = 2$ Hz)] together with signals attributable to the PH$_2$Ph ligands. In particular, a large $J(\text{PH})$ coupling constant of 347 Hz was seen for the phosphorus bound hydrogens. After 4 h, a low frequency signal [â -12.04 (d, 1H, $J(\text{PH}) = 37.5$ Hz)] associated with the hydride of 1 grew in. Other signals due to the Cp and phosphide ligand of 1 also appeared at the same rate while those due to 4 disappeared. Despite the formation of other minor products, orange 1 was easily isolated upon completion of the reaction.

As reported previously [9], the $^1$H NMR spectra of complex 1 are temperature dependent. At low temperatures (below -20°C) two sharp cyclopentadienyl signals are seen, consistent with a transoid geometry isostructural with that of Cp$_2$Mo$_2$(â-H)X$_2$(CO)$_4$ [12]. On warming, the Cp peaks gradually coalesce indicating site exchange. An activation energy $\Delta G^\ddagger$ (21°C) of 62.2 $\pm$ 0.6 kJ mol$^{-1}$ can be calculated for this process [13].

The $^{13}$C NMR spectrum of 1 in C$_6$D$_5$CD$_3$ is also temperature dependent. Again the coalescence of the two Cp resonances was seen. More interestingly, the four carbonyl resonances that are observed at $-40$°C [â 235.6 (CO); 236.8 (CO); 241.6 (d, $J(\text{PC}) = 20.5$ Hz, CO); 242.7 (d, $J(\text{PC}) = 24$ Hz, CO)] collapse to a single broad signal [â 238.2 (CO)] at 50°C. Further heating of the sample was not possible due to decomposition. The value of $\Delta G^\ddagger$ estimated either from the width of the Cp resonance after coalescence or from coalescence temperature (50°C) of the CO signals is 60 $\pm$ 2 kJ mol$^{-1}$. Since this value is the same within experimental error as determined from the proton spectra, we conclude that the same processes are involved in averaging the CO or Cp environments.

Without the benefit of the high temperature $^{13}$C NMR results, previous workers ascribed the fluxional process to isomerizations occurring via the trigonal bipyramidal (TBP) intermediates shown in Scheme 1 [9]. In the high temperature limit, this
Scheme 1.

Isomerization averages the environments of the CO groups into pairs (a ↔ d, c ↔ b) as well as making the Cp groups equivalent.

In a classic study of the fluxional behavior of CpMo(CO)$_2$XR complexes (X = phosphine or phosphite, R = H or alkyl), Faller and Anderson showed that these complexes undergo degenerate cis ↔ cis isomerizations as well as cis ↔ trans isomerizations [14]. They further showed that these isomerizations most likely occur via TBP intermediates, and that such intermediates with CO in an axial position (i.e. trans to the Cp group) are some 13–17 kJ mol$^{-1}$ higher in energy than those with X or R groups in the axial position. Rearrangement pathways leading to the trans isomers also had higher activation energies than the cis ↔ cis pathways. The interconversions shown in Scheme 1 are thus consistent with Faller and Anderson's results, but are insufficient to account for the observed high temperature limiting spectra.

The symmetry elements in the time averaged structure consist of a $C_2$ axis passing through the bridging atoms, P and H, and a mirror plane perpendicular to this axis and containing the Mo–Mo bond. Therefore, the $\mu$-P and $\mu$-H must interchange places and the RPH group must also "rotate" such that R and H become averaged. These averaging motions require that the P atom undergo inversion of configuration (e.g. 5 → 6 → 7 in Scheme 2) if high energy intermediates with carbonyl groups in the axial positions are avoided. Since the observed activation energies are similar to those measured by Faller for cis ↔ cis isomerizations, we conclude that axial P or H atoms are present in the intermediates as shown in Scheme 2. Although there exist many possible variations of the details, the fluxional process must entail the essential features shown in the scheme.

Compound 1 showed little reactivity towards traditional cluster synthons such as Co$_2$(CO)$_8$ or Cp$_2$Ni. However, the hydride in 1 is markedly acidic. In the presence of D$_2$O and NEt$_3$ in CDCl$_3$, extensive deuterium for hydrogen exchange was noticeable after 1 h by $^1$H NMR spectroscopy. In fact, 1 was readily deprotonated with $^n$BuLi in THF (tetrahydrofuran) at −80°C to form the purple anion [Cp$_2$Mo$_2$(μ-PHPh)(CO)$_4$]$^-$ (8). Solutions of 8 are exceedingly air and moisture sensitive. For example, the IR spectrum of 8 in dry, anerobic cells showed only two
bands $[\nu$(CO) (THF): 1807s, 1717s cm$^{-1}$], while the presence of even traces of air leads to the observation of multiple peaks $[\nu$(CO) (THF): 1882m, 1841s, 1797s, 1775m cm$^{-1}$]. The $^1$H NMR spectrum of the THF reaction mixture showed a single peak each for the Cp $[\delta$ 4.72 (s, 5H)] and P–H protons ($\delta$ 6.12) suggesting that only one product was formed and that the bridging hydride is removed by base. Collaborative evidence for the formation of 8 was available via protonation of solutions of the anion with acetic acid; the hydride I was recovered in very high yield (89%). Reaction of 8 with CD$_3$CO$_2$D resulted in 60% deuterium incorporation into the hydride. The $^2$H NMR of 1-D$_1$ in CHCl$_3$ showed a single phosphorus-coupled, low frequency signal $[\delta$ -11.88 (d, $J$(PD) = 49.5, $\mu$-D)] assigned to the bridging deuteride. Reaction of the anion 8 with transition metal halides, Ph$_2$I or MeI led only to low yields of 1 or (for MeI) CpMoMe(CO)$_3$.

The complex 1 reacted with [Ph$_3$C][PF$_6$] in CH$_2$Cl$_2$ to give a new species by IR spectroscopy $[\nu$(CO) (CH$_2$Cl$_2$): 1947s, 1887s cm$^{-1}$] along with some decomposition. Extensive recrystallization allowed the isolation of the new species Cp$_2$Mo$_2$(\mu-H)(\mu-PFPh)(CO)$_4$ (9). Presumably, the fluoride in 9 originated from the PF$_6^-$ counter anion. Certainly in situ generation of PF$_5$ would account for the decomposition observed in the reaction mixture. The hydride in 9 resonates at $\delta$ -10.95, a frequency about 1 ppm higher than that for 1, as a consequence of the presence of the inductively electron withdrawing fluorophosphide. Compound 9 is fluxional. The mechanism of fluxionality is probably identical to that of 1. A line
shape analysis gave an activation barrier of $\Delta G^\ddagger$ (21°C) = 59.2 ± 0.6 kJ mol$^{-1}$, comparable to that for 1.

**Experimental section**

**General data**

Infrared spectra were recorded on a Nicolet 5DX spectrometer. Proton (300.1 MHz) and $^{13}$C (75.5 MHz) NMR spectra were recorded on a Bruker AM-300 instrument. Deuterium (55.3 MHz) NMR spectra were obtained on a Bruker WM-360. Probe head temperatures were measured before and after the data acquisition with a copper-constantan thermocouple. All coupling constants are in Hertz. Mass spectra were recorded on VG-70-250-S mass spectrometer using either EI or FAB ionization modes. Elemental analyses were performed by the University of Michigan microanalytical service. All operations were performed under a nitrogen atmosphere using rigorously dried and deoxygenated solvents with standard Schlenk techniques. The compound Cp$_2$Mo$_2$(CO)$_6$ was prepared by known procedures [15]. Phenylphosphine, $^n$BuLi, and [Ph$_3$C][PF$_6$] (Aldrich) were used as supplied.

**Preparation of Cp$_2$Mo$_2$(CO)$_4$(PH$_2$Ph)$_2$ (4)**

The dimer Cp$_2$Mo$_2$(CO)$_4$ (4.00 g, 8.16 mmol) was suspended in toluene (150 mL) and the suspension refluxed (16 h) with a slow nitrogen purge. The resulting solution of Cp$_2$Mo$_2$(CO)$_4$ (Mo=Mo) was allowed to cool to ambient temperature and filtered to remove insoluble material. Neat PH$_2$Ph (1.85 mL, 1.85 g, 16.81 mmol) was added and the mixture stirred (15 min). The red Cp$_2$Mo$_2$(CO)$_4$(PH$_2$Ph)$_2$ (4) was collected by filtration and washed with hexane (3 x 15 mL). Concentration of the mother liquors to ca. 50 mL afforded a second crop. Total yield of red Cp$_2$Mo$_2$(CO)$_4$(PH$_2$Ph)$_2$, was 3.68 g (69%). Anal. Found: C, 47.82; H, 3.68. C$_{26}$H$_{24}$Mo$_2$O$_4$P$_2$ calc.: C, 47.72; H, 3.70%. IR (CH$_2$Cl$_2$): $\nu$(CO) 1862sh, 1844s cm$^{-1}$. $^1$H NMR (CDCl$_3$, 20°C): $\delta$ 4.83 (d, 1OH, J(PH) = 2, Cp); 6.31 (d, 4H, J(PH) = 347, PH$_2$); 7.39-7.51 (m, 6H, Ph-); 7.60-7.72 (m, 4H, Ph-ol. 13C NMR (CDCl$_3$, 20°C): $\delta$ 90.7 (Cp), 128.7 (d, J(PC) = 10, Ph-m); 130.0 (Ph-p); 132.0 (d, J(PC) 10, Ph-o); 232.6 (d, J(PC) = 26, CO). Due to an inadequate signal-to-noise ratio the Ph-i signal was not detected. Poorly soluble 4 does not form concentrated solutions. Mass spectrum (EI): m/z 544 [(M – PH$_2$Ph)$^+]$.

**Preparation of Cp$_2$Mo$_2$(μ-H)(μ-PHPPh)(CO)$_4$ (1)**

A suspension of Cp$_2$Mo$_2$(CO)$_4$(PH$_2$Ph)$_2$ (4) (1.30 g, 1.99 mmol) in toluene (100 mL) was stirred (16 h) at room temperature after which time an orange solution had formed. The solvent was removed and the residue extracted with CH$_2$Cl$_2$ (3 x 50 mL). The extracts were filtered through an Al$_2$O$_3$ plug and the solvent removed. The orange residue was recrystallized from CH$_2$Cl$_2$/hexane to yield orange crystals of Cp$_2$Mo$_2$(μ-H)(μ-PHPPh)(CO)$_4$ (1) (0.71 g, 65%). This reaction was not reversible; no reaction of 1 with excess PH$_2$Ph was observed.

Alternatively, the adduct 4 may be prepared in situ by adding 2 equiv. of PhPH$_2$ to Cp$_2$Mo$_2$(CO)$_4$ [16] in toluene and stirring or refluxing the resultant suspension of 4. Anal.: Found: C, 43.99; H, 3.15. C$_{26}$H$_{17}$Mo$_2$O$_4$P calc.: C, 44.14; H, 3.15%. IR (CH$_2$Cl$_2$): $\nu$(CO) 1940s, 1871s cm$^{-1}$. $^1$H NMR (CDCl$_3$, –40°C): $\delta$ = 12.04 (d, 1H,
$J(\text{PH}) = 37.5$, $\mu$.H); 5.03 (s, 5H, Cp); 5.18 (s, 5H, Cp); 6.53 (d, 1H, $J(\text{PH}) = 354$, PH); 7.24–7.39 (m, 5H, Ph). $^{13}$C NMR (CDCl$_3$, $-40^\circ$C): $\delta$ 90.38 (Cp); 91.52 (Cp); 128.0 (d, $J(\text{PC}) = 10.5$, Ph-m); 128.9 (Ph-p); 139.7 (d, J(Ph) = 10, Ph-o); 139.7 (d, J(Ph) = 38, Ph-i); 234.6 (CO); 236.1 (CO); 242.0 (d, J(Ph) = 21, CO); 242.9 (d, J(Ph) = 24, CO). Mass spectrum (EI): $m/z$ 544 [M$^+$].

**Preparation of [Cp$_2$Mo$_2$(μ-PPh)(CO)$_4$]$^-$(8)**

$^8$BuLi (0.1 mL of 1.76 M hexane solution, standardized by titration, 0.18 mmol) was added to a solution of 1 (0.10 g, 0.18 mmol) in THF at $-80^\circ$C. The mixture was allowed to come to room temperature (1 h) during which time it became purple. Such solutions were generally used without further purification. When Et$_2$O containing 12-crown-4 was used as solvent, somewhat impure [Li(12-crown-4)]Cp$_2$Mo$_2$(μ-PPh)(CO)$_4$, (Li(12-crown-4)8) precipitated in quantitative yield upon addition of the $^8$BuLi. IR (THF): $\nu$(CO) 1807s, 1717s cm$^{-1}$. $^1$H NMR (CDCl$_3$, THF, 20°C): $\delta$ 4.72 (s, 5H, Cp). $^1$H NMR [Li(12-crown-4)8, CD$_3$CN, 20°C]: $\delta$ 3.64 (s, 16H, 12-crown-4); 4.83 (s, 5H, Cp); 6.12 (d, 1H, $J(\text{PH}) = 272$, PH); 7.13–7.23 (m, 3H, Ph-m + p); 7.30–7.37 (m, 2H, Ph-o).

**Reaction of [Cp$_2$Mo$_2$(μ-PPh)(CO)$_4$]$^-$(8) with MeCO$_2$H**

A solution of the anion 8 (0.18 mmol) was prepared as above and cooled to $-80^\circ$C. One drop of MeCO$_2$H was added and the reaction allowed to come to room temperature (1.5 h) during which time it became orange. The solvent was removed and the residue recrystallized from CH$_2$Cl$_2$/hexane to yield Cp$_2$Mo$_2$(μ-H)(μ-PPh)(CO)$_4$ (1) as orange crystals, 89 mg (89%). Similar reaction of 8 with CD$_3$CO$_2$D gave an equally high yield of a mixture of 1 and 1-D$_1$ in a 40:60 ratio.

**Preparation of Cp$_2$Mo$_2$(μ-H)(μ-PFPh)(CO)$_4$ (9)**

Solid [Ph$_3$C][PF$_6$] (0.14 g, 0.36 mmol) was added to a solution of 1 (0.20 g, 0.36 mmol) in CH$_2$Cl$_2$ (25 mL) at room temperature. The reaction mixture darkened and the IR spectrum [(CH$_2$Cl$_2$): $\nu$(CO) 1947s, 1887s cm$^{-1}$] indicated the formation of a new species. The mixture was filtered through Celite and the solvent removed. Repeated recrystallization from CH$_2$Cl$_2$/hexane afforded a small amount of orange crystalline 9, 22 mg, 11%. Anal. Found: C, 42.86; H, 2.82. C$_{20}$H$_{16}$FMo$_2$O$_4$P calc.: C, 42.72; H, 2.87%. IR (CH$_2$Cl$_2$): $\nu$(CO) 1947s, 1887s cm$^{-1}$. $^1$H NMR (CDCl$_3$, $-40^\circ$C): $\delta$ –10.95 (d, 1H, $J(\text{PH}) = 41$, m-H); 5.01 (s, 5H, Cp); 5.32 (s, 5H, Cp); 7.19 –7.49 (m, 5H, Ph). Mass spectrum (EI): $m/z$ 562 [M$^+$].

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**References**