

Chemistry of the thermally generated, molybdenum-centered radicals $\{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{L}\}$ ($\text{L} = \text{CO}, \text{PPh}_3$)

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Abstract

In contrast to their chromium analogues, the compounds $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{L}]_2$ ($\text{L} = \text{CO}, \text{PPh}_3$) exist in solution solely as the metal–metal bonded dimers, no chemical evidence being found for the presence of small equilibrium amounts of the corresponding monomers $\{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{L}\}$. However, the latter are readily synthesized via hydrogen atom abstraction by the trityl radical from the hydrides $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{LH}$. The thus-formed radicals are very reactive and, as well as dimerizing, they take part in a variety of atom abstraction and ligand substitution reactions. Analysis of the product distributions of these reactions provides clear evidence for the intermediacy of seventeen-electron intermediates.

There has recently been growing interest in the chemistry of seventeen-electron organotransition metal compounds. Such species can be synthesized via either photolysis of metal–metal bonded eighteen-electron dimeric compounds [1] or via electron transfer reactions of eighteen-electron monomers [2], and have also been proposed as intermediates in a variety of reactions involving organometallic compounds [3]. They are nonetheless normally very unstable with respect to dimerization, and are only rarely found to exist under ambient conditions as persistent organometallic radicals [4].

However, recent reports have shown that the compound $[\text{CpCr}(\text{CO})_3]_2$ contains a sufficiently weak chromium–chromium bond that it dissociates spontaneously in solution to give low but chemically significant concentrations of the seventeen-electron monomer $\{\text{CpCr}(\text{CO})_3\}$ [5]. (Hereafter all metal-centered radical species will be denoted as such with brace brackets). Consistent with these observations, we have earlier found that the solution chemistry of the dimeric chromium compound actually reflects the chemistry of the monomeric species [6]. Thus $[\text{CpCr}(\text{CO})_3]_2$ generates the monomer, which in turn readily abstracts the iodine atom from methyl iodide to give $\text{CpCr}(\text{CO})_3\text{I}$ and $\text{CpCr}(\text{CO})_3\text{Me}$, or reacts with ^{13}CO and tertiary phosphines to give ^{13}CO -labelled dimer and chromium-centered radicals of the

formula $\{\text{CpCr}(\text{CO})_2\text{L}\}$ (L = tertiary phosphine), respectively. Both the atom abstraction and the ligand substitution reactions are facile, typical of seventeen-electron compounds [4].

Interestingly, except for the complex of the relatively small $\text{P}(\text{OMe})_3$, all of the known, substituted compounds $\{\text{CpCr}(\text{CO})_2\text{L}\}$ are monomeric in solution [5d,6a,6c], and it seems that steric factors may play a significant role in stabilizing this class of organometallic radicals with respect to dimerization. We have also found that the compound $[\eta^5\text{-C}_5\text{Me}_5\text{Cr}(\text{CO})_3]_2$, with the bulky C_5Me_5 group, is completely dissociated in solution [7a], and it thus seemed likely that persistent organometallic radicals of the other metals of the chromium triad may be similarly stabilized by sterically demanding ligands.

We have therefore carried out an investigation into the possibility of synthesizing a series of sterically encumbered complexes of the type $\{\text{CpMo}(\text{CO})_2\text{L}\}$ (L = bulky phosphine), and report herein the results of a series of experiments into the formation and chemistry of the non-persistent, molybdenum-centered radicals $\{\text{CpMo}(\text{CO})_2\text{L}\}$ (L = CO, PPh_3). We note that a related persistent radical, $\{(\text{trispyrazolylborate})\text{Mo}(\text{CO})_3\}$, has been reported recently [7b].

Experimental

Instrumentation. Infrared spectra were recorded on a Bruker IFS-85 FTIR spectrometer, ^1H NMR spectra on Bruker HX60 and AM400 FTNMR spectrometers.

The compounds $[\text{CpMo}(\text{CO})_2(\text{PPh}_3)]_2$ [8*], $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)$ [8*], $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{Cl}$ [9*], $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{I}$ [9*], $\text{CpMo}(\text{CO})_3\text{H}$ [10*], and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ [9*] were prepared as in the literature, while triphenylmethyl chloride was reduced to $[\text{Ph}_3\text{C}]_2$ using a modification of the original Gomberg method [11a]. Typically, 0.42 g Ph_3CCl (1.5 mmol) and 0.49 g zinc dust were suspended in 20 ml benzene and stirred in the dark for at least 3 h. The solvent was then removed under reduced pressure prior to storage, or the solution of the orange-red oil was used directly.

Hydrogen abstraction reactions. In a typical procedure, a benzene solution of $[\text{Ph}_3\text{C}]_2$, prepared as above, was added at room temperature to a stirred benzene solution of 1.0 mmol $\text{CpMo}(\text{CO})_2\text{LH}$ (L = CO, PPh_3), sometimes in the presence of added phosphine. The reaction mixture was stirred in the dark at room temperature for 15 min, the course of the reaction being monitored by IR spectroscopy. Removal of the solvent then made possible further characterization of the products by NMR spectroscopy although, in cases of mixtures, products were first separated by elution of a 1/1 hexanes/ CH_2Cl_2 solution through an alumina column.

Results and discussion

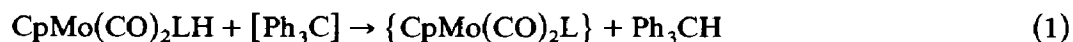
Anticipating that sterically crowded complexes of the type $[\text{CpMo}(\text{CO})_2\text{L}]_2$ might, like $[\text{CpCr}(\text{CO})_3]_2$, dissociate spontaneously in solution to form significant amounts of relatively reactive monomers, we carried out an experiment in which

* Reference number with asterisk indicates a note in the list of references.

$[\text{CpMo}(\text{CO})_2(\text{PPh}_3)_2]$ [8*] was treated at room temperature in THF solution with a five-fold molar excess of methyl iodide as a spin trap. By analogy with the chemistry of $[\text{CpCr}(\text{CO})_3]_2$, it was anticipated that $\{\text{CpMo}(\text{CO})_2(\text{PPh}_3)\}$ radicals formed from thermal dissociation of $[\text{CpMo}(\text{CO})_2(\text{PPh}_3)_2]$ would react to form equimolar quantities of the compounds $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{Me}$ and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{I}$.

The investigation seemed promising initially, as a good yield of the compound $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{I}$ [9*] was obtained. No methyl-molybdenum compound was formed, however, reminiscent of many similar photochemical processes [1], and it was then determined that the reaction did not proceed in the dark. Thus, while a reaction of the molybdenum-centered radical had been observed, the radical was formed photolytically (fluorescent lights) rather than thermally, as desired.

We then assessed the possible utilization of the trityl radical, $[\text{Ph}_3\text{C}]$, to abstract hydrogen atoms from molybdenum hydrides and generate molybdenum-centered radicals as in eq. 1.

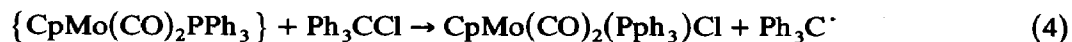


This type of atom abstraction reaction has been reported to occur with $\text{HCo}(\text{CO})_4$, to yield Ph_3CH and $\text{Co}_2(\text{CO})_8$ [12a], and with $\text{CpW}(\text{CO})_3\text{H}$ in the presence of Ph_3CCl and tertiary phosphines L to form $\text{CpW}(\text{CO})_3\text{Cl}$ and $\text{CpW}(\text{CO})_2\text{LCl}$ [12b]. In both cases, metal radical intermediates were believed to be involved.

Care had to be taken to prepare the radical dimer as described, as refluxing the solution during the synthesis resulted in significant deterioration of the product [11b] while stirring under the fluorescent lights resulted in significant loss by disproportionation [11c]. The trityl dimer was generally characterized by resonances in the ^1H NMR spectrum (C_6H_6) at δ 7.37 (m, 15H), δ 5.4–6.6 (dd, 4H), δ 5.02 (s, 1H) [11d]. It dissociates at room temperature to an extent of 2–2%, with a half-life of the order of 0.4 min [11e].

Benzene solutions of the hydrides $\text{CpMo}(\text{CO})_3\text{H}$ [10*] and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ [9] were therefore treated with solutions of the trityl dimer [11] in benzene at room temperature in the dark, resulting in both cases in the yellow colour of the hydride solutions being replaced within 5 min by a deep red colour. The identities of the products were determined by IR (benzene) and ^1H NMR (benzene- d_6) spectroscopy, which showed that the major products were the dimers, $[\text{CpMo}(\text{CO})_3]_2$ [13*], or $[\text{CpMo}(\text{CO})_2(\text{PPh}_3)]_2$ [8], as well as triphenylmethane ($\delta(\text{CH})$ 5.41). The chloro compound $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{Cl}$ [9*] was also formed in the triphenylphosphine system of small amounts of Ph_3CCl were present.

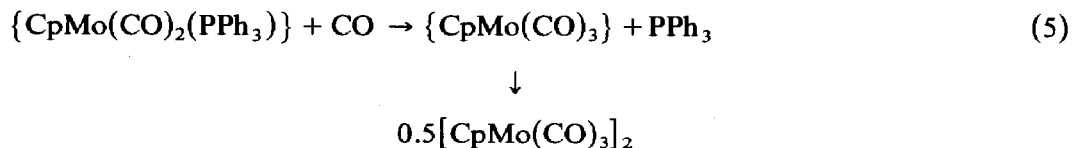
Thus it seems clear that the radicals $\{\text{CpMo}(\text{CO})_2\text{L}\}$ ($\text{L} = \text{CO}, \text{PPh}_3$) had indeed formed (eq. 2) and, as expected [1,4,12], either dimerized (eq. 3) or abstracted the chlorine atom from Ph_3CCl (eq. 4).



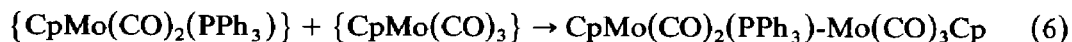
In spite of the steric requirements of the coordinated PPh_3 (cone angle 145° [14]), the metal-metal bond strength of the dimer $[\text{CpMo}(\text{CO})_2\text{PPh}_3]_2$ is sufficiently high that radical dimerization occurred spontaneously and rapidly.

Since a characteristic property of seventeen-electron complexes is that ligand substitution reactions are normally very rapid [4], a series of experiments was then carried out to ascertain if transient radicals of the type $\{\text{CpMo}(\text{CO})_2\text{L}\}$, formed as in eq. 2, would undergo ligand substitution reactions prior to dimerization or halogen abstraction from Ph_3CCl . The intermediacy of radicals could then be deduced from the nature of any products of substitution.

Although the compound $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ was shown to be inert to reaction of ^{13}CO (1 atm) over 24 h, it was found that this hydride does react with CO (normal isotopic distribution) in benzene solution within 5 min in the presence of slightly more than one equivalent of trityl dimer to form $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)$ [8*] and $[\text{CpMo}(\text{CO})_3]_2$. In the presence of 1 atm of ^{13}CO , these products are partially enriched, as shown by IR spectroscopy [15]. The conclusion to be drawn from this experiment is that hydrogen atom abstraction from $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ does indeed result in the formation of the seventeen-electron species $\{\text{CpMo}(\text{CO})_2(\text{PPh}_3)\}$ (eq. 2). However, while the latter shows a high proclivity to dimerization (eq. 3), it is exceedingly substitution-labile and, in the presence of free CO, substitution of PPh_3 occurs to give the radical $\{\text{CpMo}(\text{CO})_3\}$, which subsequently dimerizes (eq. 5).

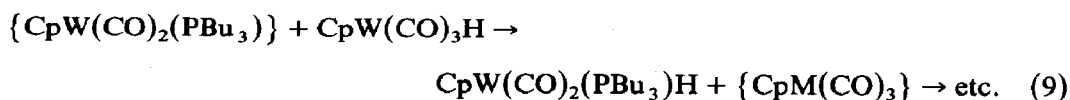


The mono-phosphine product results similarly from coupling of the substituted and the tricarbonyl radicals (eq. 6).



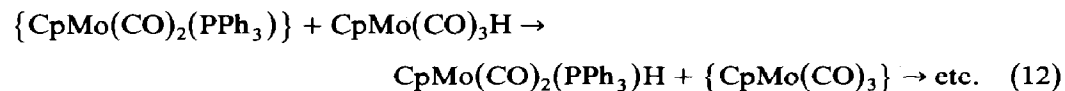
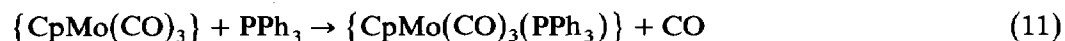
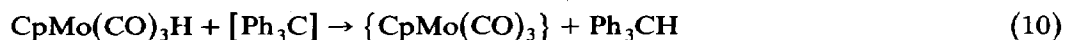
We also carried out an experiment in which a benzene solution of $\text{CpMo}(\text{CO})_3\text{H}$ was treated with PPh_3 , in the dark and in the presence of one equivalent of trityl dimer. Although $\text{CpMo}(\text{CO})_3\text{H}$ reacts slowly with PPh_3 under these conditions in the absence of trityl radical, reaction in the presence of added trityl dimer was complete within 5 min, giving the compounds $[\text{CpMo}(\text{CO})_3]_2$, $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{PPh}_3$ and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$. While the formation of the first two species can be rationalized on the basis of arguments presented above, formation of the substituted hydride requires further comment.

Hoffman and Brown have studied the kinetics of the thermal substitution of CO in the compound $\text{CpW}(\text{CO})_3\text{H}$ by PBu_3 [16]. It was found that the rate law was best accommodated by a series of steps as follows:



Thus a chain radical process is involved in the substitution reaction of $\text{CpW}(\text{CO})_3\text{H}$; by analogy, formation of the compound $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ during the hydrogen abstraction reaction of $\text{CpMo}(\text{CO})_3\text{H}$ in the presence of triphenyl-

phosphine presumably also involves the intermediacy of both the substituted and the tricarbonyl molybdenum radicals, as shown in eqs. 10–12.



Interestingly, if the above abstraction reaction is carried out in the presence of two equivalents of trityl dimer, the only products are the compounds $[\text{CpMo}(\text{CO})_3]_2$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{PPh}_3$; no hydride $\text{CpMo}(\text{CO})_2\text{PPh}_3\text{H}$ is formed. The most appealing rationale for this observation is that, in the presence of higher concentrations of trityl radical, formation of the tricarbonyl radical $\{\text{CpMo}(\text{CO})_3\}$ occurs more rapidly and the bimolecular coupling reactions become more competitive than CO substitution by PPh_3 . A secondary reaction involving hydrogen atom abstraction from the hydride $\text{CpMo}(\text{CO})_2\text{PPh}_3\text{H}$ clearly does not pertain, as none of the dimer expected from this reaction is formed.

Acknowledgements

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