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THE LEWIS BASICITY OF TRANSITION METALS. REACTIONS OF THE GROUP VIB TRIPHENYLPHOSPHONIUM (TRICARBONYLMETAL)CYCLOPENTADIENYLIDES WITH TRIFLUOROACETIC ACID AND BORON TRIFLUORIDE

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SUMMARY

The triphenylphosphonium (tricarbonylchromium)-, (tricarbonylmolybdenum)- and (tricarbonyltungsten)cyclopentadienylides dissolve readily in trifluoroacetic acid to give highly colored solutions. Their proton NMR spectra exhibit a high field line (τ 15–18) which is characteristic of the $M-H^+$ group. This line shifts upfield, and the multiplets for the C_5H_4 ring shift downfield, with increasing metal atomic weight. These results suggest that an increasingly greater amount of electron density is shifted to the attached proton as the metal atomic weight increases; it is argued that this is indicative of the increasing Lewis basicity of the transition metals in these compounds. Boron trifluoride also reacts readily with the molybdenum and tungsten compounds and to some extent with the chromium compound. Although complicating factors were observed, elemental analyses and studies of the chemical and physical properties of the deep red solid products suggest that they are 1/1 Lewis acid–base adducts, $Ph_3PC_5H_4M(CO)_3 \cdot BF_3$; it is thought that the metal is again acting as the basic site. Tensimetric titrations of the triphenylphosphonium(tricarbonylmetal)-cyclopentadienylides, as well as qualitative observations, also suggest that the Lewis basicity of the transition metals increases in the order $Cr < Mo < W$. BCl_3 undergoes a 1/1 reaction with the Cr and Mo compounds, but diborane does not react with the Mo compound.

INTRODUCTION

The first confirmed example of a transition metal in a neutral compound acting as a Lewis base was reported in 1955[1,2]. Wilkinson and Birmingham found that di-π-cyclopentadienylrhenium hydride could be protonated in dilute aqueous acid. This report led to studies on the Group VIB di-π-cyclopentadienylmetal dihydrides[3], arenechromium tricarbonyls[4], and other organometallic compounds[4] in an attempt to clarify the factors which would lead to metal protonation. These developments were followed by Shriver's discovery that Cp_2WH_2 formed a 1/1 adduct with BF_3[5], and

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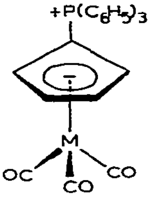
Parshall's work on the interaction of diborane with the carbonyl anions of rhenium, manganese, and cobalt[6]. Perhaps the best characterized examples of transition metal Lewis basicity are provided by the mercuric halide complexes of π-cyclopentadienylcobalt dicarbonyl[7]. Many other compounds are now known to be protonated in strongly acidic media or react with inorganic Lewis acids; these and other aspects of transition metal Lewis basicity have been reviewed recently[8].

Early in our studies on the interactions of boron compounds with transition metal compounds we discovered that the Group VIB triphenylphosphonium (tricarbonylmetal)cyclopentadienylides* (I) (the ylid ligand $Ph_3PC_5H_4$ is henceforth



(I)

abbreviated Cpylid) underwent a very ready reaction with boron trihalides. Our first thought was that the metals acted as the site of Lewis basicity and formed a donor–acceptor complex with the boron compound. Therefore, in order to discover whether or not the metal atom in these complexes could act as a Lewis base, we examined the NMR and IR spectra of the Cpylidmetal tricarbonyls in trifluoroacetic acid. The first part of this paper discusses the protonation studies, and the second part is concerned with our observations on the boron trihalide reactions.

RESULTS AND DISCUSSION

Reaction with trifluoroacetic acid

All three of the yellow Cpylidmetal tricarbonyls dissolve readily in trifluoroacetic acid (TFA) to give highly colored solutions. IR and NMR data for these acid solutions are given in Table 1.

NMR spectra of all three compounds in TFA show a high field line (τ 15–18) which is characteristic of a hydrogen atom or proton attached to a transition metal. The spectrum of the tungsten complex (Fig. 1) in TFA is typical of all three complexes. The resonance lines for $M-H^+$ were very sharp (*ca.* 1 Hz at half-height), thus ruling out strong spin-coupling between the C_5H_4 group and $M-H^+$. More importantly, $^{183}W-H$ spin-coupling was observed; this is more conclusive proof that the proton is attached directly to the metal and that proton exchange between the complex and TFA is slow. It might be noted that the J-value for $^{183}W-H$ coupling (36 Hz) is very similar to that observed for $CpW(CO)_3H$ and $Cp_2W_2(CO)_6H^+$ (refs. 9 and 4).

Further evidence that the proton is probably attached to the metal was obtained by IR spectroscopy. It was anticipated that protonation of these complexes would lead to an increase in the frequency of the CO stretching vibrations. Such an effect has been observed for, *inter alia*, $(Ph_3P)_2Fe(CO)_3$ and $(Ph_3P)Fe(CO)_4$ upon protonation[4] and for mercuric halide adducts of organometal carbonyls[7,10]. The data

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* [(Tricarbonylmetal)cyclopentadienylene]triphenylphosphoranes.

TABLE 1

NMR AND IR DATA FOR THE GROUP VIB CYCLOPENTADIENYLMETAL TRICARBONYL HYDRIDES, CPYLIDMETAL TRICARBONYLS, AND THE PROTONATED CPYLIDMETAL TRICARBONYLS

Compound	M	$\tau(C_5H_n)$ (ppm)	τ(MH) (ppm)	ν(CO) (cm^{-1})
$CpM(CO)_3H^a$	Cr	5.22	15.46	
	Mo	4.70	15.52	2072 vs, 2020 (sh), 1940 vs, 1904 m
	W	4.65	17.33^b	2026 vs, 2016 (sh), 1935 vs, 1900 (sh)
$CpylidM(CO)_3^c$	Cr	5.08, 5.35^d		1913 s, 1806 vs
	Mo	4.51, 4.77^d		1920 s, 1812 vs
	W	4.51, 4.78^d		1912 s, 1802 vs
$[CpylidM(CO)_3H]^{+e}$	Cr	4.58, 4.80^d	15.09	2042 s, 1962 vs (br)
	Mo	4.09, 4.31^d	15.34	2048 s, 1970 vs (br)
	W	4.00, 4.27^d	17.15^f	2042 s, 1958 vs (br)

[a] See ref. 9; all data obtained for hexane solutions. [b] $J(^{183}W-^1H)$ 37.7 Hz. [c] All data obtained in $CHCl_3$. [d] Two, four line multiplets typical of an A_2B_2 spectrum; $J \simeq 2.5$ Hz. [e] All data obtained in CF_3COOH. The shift for the most prominent line of the multiplet due to the PPh_3 group in all three compounds is *ca.* τ 2.15. [f] $J(^{183}W-^1H) = 36$ Hz.

in Table 1 indicate that the expected high frequency shift was observed, and that the parent molecules and protonated complexes display only two bands. When the tungsten compound was dissolved in deuterotrifluoroacetic acid, the spectrum in the 2100–1850 cm^{-1} region was identical to that observed in normal TFA. Therefore, both bands are due to CO stretching modes; the $M-H^+$ stretch was not located.

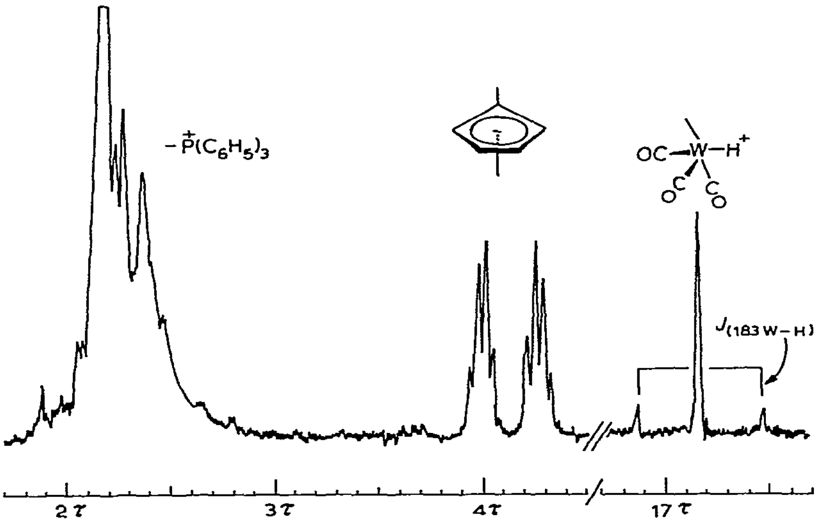
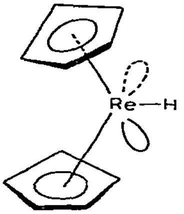
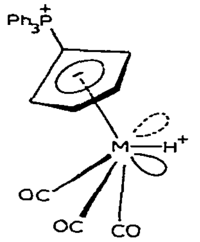


Fig. 1. ^1H NMR spectrum of $(C_6H_5)_3PC_5H_4W(CO)_3$ in CF_3COOH. See Table 1 for chemical shifts.

One of the first questions which must be answered is why the Cpylidmetal tricarbonyls should undergo protonation in strong acid media. Intimately associated with this question is that of the probable structure of the protonated complex. Dahl and Ballhausen developed a theory for bonding in the di-π-cyclopentadienylmetal hydrides[11]; that theory may be applied qualitatively in this instance. In the former case, Dahl and Ballhausen showed that three strongly space directed orbitals remain on the metal after accounting for primary ring–metal bonding; two of the three orbitals contain a pair of electrons and the third is used to bond to the attached hydrogen. The structural consequence of such bonding is that the rings are not parallel as in ferrocene (II). Green has pointed out that the Dahl–Ballhausen theory may be extended to include carbonyl complexes, since "the three carbonyl groups may be regarded as having steric and electronic effects similar to those of a π-cyclopentadienyl group[12]". In the case of the Cpylidmetal tricarbonyls, there are six valence electrons left on the metal after accounting for primary metal–ring and metal–CO bonding. The proton may be bonded to the metal, therefore, by utilizing one pair of these electrons, the resulting structure being approximately as depicted by (III).



(II)



(III)

There are two outstanding features of the data in Table 1: (1). The M–H resonance line shifts upfield with increasing metal atomic weight for both the cyclopentadienylmetal tricarbonyl hydrides and the isoelectronic protonated Cpylidmetal tricarbonyls. (2). There is also a downfield shift of the cyclopentadienyl protons with increasing metal atomic weight in both series of compounds. Upon protonation, the cyclopentadienyl protons of all three Cpylidmetal tricarbonyls shift downfield by about 0.5 ppm.

Ginsberg has pointed out that, for a given transition metal group, the chemical shift for M–H generally decreases on proceeding from the first to the second period, and then increases on passing to the third period[13]. The values of τ(M–H) for the two isoelectronic series in Table 1 are exceptions to this generalization. The reasons for this trend in the Group VIB cyclopentadienylmetal tricarbonyl hydrides were examined theoretically by Lohr and Lipscomb[14]. They found that about 90% of the high field shift for M–H is due to the presence of an excess of negative charge on the hydrogen, and the increase in τ(M–H) with increasing metal atomic weight is due to increasing electron density on the hydrogen. Since the protonated Cpylidmetal tricarbonyls are isoelectronic with the cyclopentadienylmetal tricarbonyl hydrides, it does not seem unreasonable to assume that the increase in τ(M–H) with increase in metal atomic weight is also due to an increase in negative charge on the attached proton*.

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* Although there is a striking similarity in the τ(M–H) values for corresponding compounds in the two isoelectronic series, a direct comparison of absolute shift values is unjustified, the two series of compounds having been run in different solvents. However, we do not believe that this invalidates a comparison of the *trends* in τ(M–H) values for the two series.

The coordinating strength of a Lewis base is best defined in thermodynamic terms[15]. It has also been shown to be related directly to the amount of charge transferred from a Lewis base to a Lewis acid[16]. Since the chemical shift of $M-H^+$ in the protonated Cpylidmetal tricarbonyls increases with increasing metal atomic weight, and since this increase is probably due to increased charge density on the attached "proton," we are led to the conclusion that the Lewis basicity of the Group VIB metals *in these compounds* increases with increasing metal atomic weight.

The nucleophilicity of an anion or neutral compound is a kinetic quantity; that is, it is related to the rate at which a nucleophile reacts with a given electrophilic reagent. Although nucleophilicity and basicity are not necessarily related, it is apparent that they may be for the Group VIB cyclopentadienylmetal tricarbonyl anions. An increase in nucleophilicity with increasing metal atomic weight was found for these anions[17]. Therefore, the anion nucleophilicity parallels $\tau(M-H)$ for the protonated anions, the cyclopentadienylmetal tricarbonyl hydrides.

From the above discussion, it seems reasonable to conclude that the Lewis basicity of the Group VIB metals increases with increasing metal atomic weight in the two isoelectronic series, $CpM(CO)_3^-$ and $CpylidM(CO)_3$. However, good correlations between $\tau(M-H)$ and anion nucleophilicity do not always hold for other series of compounds. For the isoelectronic series of carbonyl anions, $Co(CO)_4^-$, $Mn(CO)_5^-$, and $Re(CO)_5^-$, the nucleophilicity of the anions[17], borane adduct stability[6], and acid ionization constants[18], all indicate an increase in Lewis basicity with increasing metal atomic weight*. However, $\tau(M-H)$ for the carbonyl hydrides decreases with increasing metal atomic weight[19].

King has recently demonstrated that the chemical shift of the π-cyclopentadienyl group in π-cyclopentadienylmetal carbonyl compounds reflects the negative charge on the transition metal, high field shifts being indicative of a relatively high negative charge[20]. For the cyclopentadienylmetal tricarbonyl hydride series, the resonance line for the π-C_5H_5 group shifts downfield as the metal is changed from Cr to W. One would predict, therefore, that the chromium atom is more negatively charged in its compound than the tungsten atom. Lohr and Lipscomb's calculations confirm this prediction, the following charges having been calculated: Cr, -0.76; Mo, $+0.14$; W, $+0.92$**. Upon protonation of the Cpylidmetal tricarbonyls, the metal atoms would be expected to become more positive; forward σ and π bonding from the C_5H_4 group should increase and retrodative δ bonding should decrease. The resonance lines for the C_5H_4 should therefore shift to lower fields as observed.

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* Anders and Graham[35] have pointed out that, although carbonyl anions such as $Co(CO)_4^-$ do not have stereochemically active lone pairs of electrons, it is nonetheless useful to think of them as Lewis bases in their reactions.

** Lohr and Lipscomb also report charges on the π-C_5H_5 group; Cr, -0.90; Mo, -1.41; W, -2.41[14]. They stated that this suggested "successively greater ring-proton shifts to high field in accord with the observed absolute chemical shifts for the ring protons of 29.78, 30.30, and 30.35 ppm for Cr, Mo, and W, respectively". (Reference point for absolute shifts is the bare proton at about -35 ppm from TMS.) The source of their data was given as ref. 9, the same source from which the data in Table 1 was taken; the ring proton shifts reported by Lohr and Lipscomb are contrary to those in ref. 9. Therefore, the calculated charges predict a result opposite to that observed. The reasons for the anomalous statement in Lohr and Lipscomb's paper are not clear.

Boron trihalide reactions

Methylene chloride solutions of the Cpylidmetal tricarbonyls were tensimetrically titrated with BF_3 at 0° and −78° (Fig. 2 and 3). As BF_3 was added to the molybdenum and tungsten compounds in particular, the yellow starting material dissolved to give solutions which became progressively more red and less yellow. The titration curves suggest that the reaction between the metal compound and BF_3 is reversible. At any point along the curve for a particular compound, the temperature

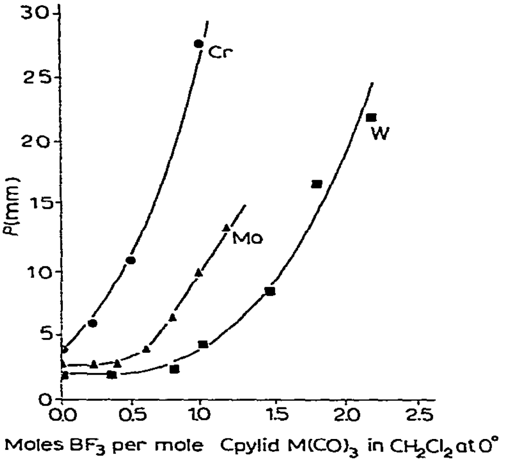


Fig. 2. Tensimetric titration curves for the reaction of BF_3 with the Group VIB triphenylphosphonium (tricarbonylmetal)cyclopentadienylides at 0°. The curves have been separated for clarity. To obtain the true pressure, add 140 mm to the Cr curve, 141 mm to the Mo curve, and 142 mm to the W curve.

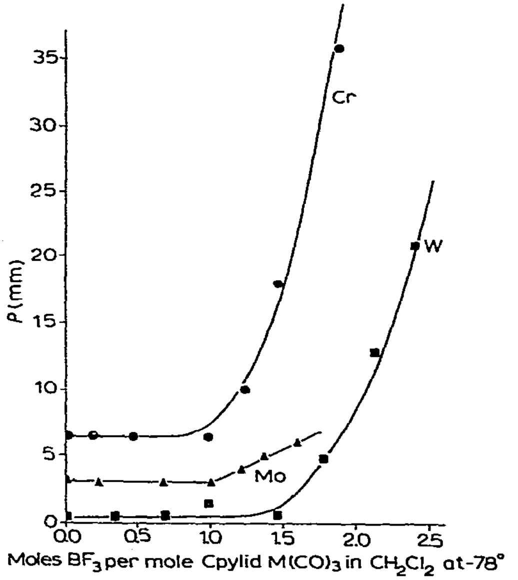


Fig. 3. Tensimetric titration curves for the reaction of BF_3 with the Group VIB triphenylphosphonium (tricarbonylmetal)cyclopentadienylides at −78°. The curves have been separated for clarity. To obtain the true pressure, subtract 5 mm from the Cr curve and 2 mm from the Mo curve.

could be changed back and forth between 0° and $-78°$; the vapor pressure appropriate to either temperature did not change noticeably over the period of about one hour. Furthermore, when volatile materials were removed at 0° after a tensimetric titration, the IR spectrum of the red solid residue always indicated the presence of some unreacted CpylidM$(CO)_3$, even though the titration curves showed that the stoichiometry was at least 1/1 for all three compounds at $-78°$. These IR spectra also showed new carbonyl bands, as well as a broad band at 1050 cm^{-1}; this latter band is usually characteristic of coordinated BF_3 or BF_4^- (refs. 5 and 21).

A sample of the product from the CpylidMo$(CO)_3$/BF_3 reaction was examined by thin layer chromatography; a CH_2Cl_2/THF mixture was used as the eluting solvent. This experiment indicated that a small amount of a brown material was present in addition to a red solid and starting material. The crude solid was purified by recrystallizing it rapidly from CH_2Cl_2 and toluene or by washing with THF; in both instances some product was lost due to dissociation.

The purified, deep red solids from the molybdenum and tungsten reactions were air-stable. Due to almost complete dissociation on removing BF_3, no chromium-containing product could be obtained. The apparent reversibility of the BF_3 reactions, and elemental analyses (Table 3) of the molybdenum- and tungsten-containing solids, strongly suggest that they are 1/1 adducts with BF_3 (IV). This conclusion is supported by their IR spectra; not only is a band observed which may be attributed to coordinated BF_3, but the carbonyl stretching frequencies (see Table 2) have increased as they did upon protonation.

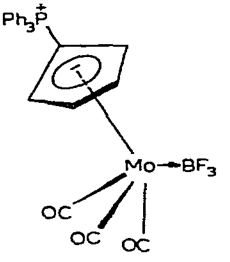
TABLE 2

IR DATA (NUJOL MULLS) FOR THE TRIPHENYLPHOSPHONIUM (TRICARBONYLMETAL)CYCLOPENTADIENYLIDES AND THEIR BORON TRIFLUORIDE ADDUCTS

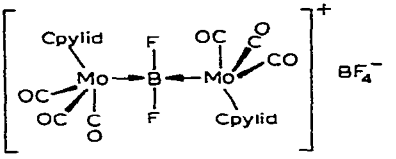
Compound	Carbonyl stretching frequencies (cm^{-1})		
CpylidCr$(CO)_3$	1900 s,	1805 vs,	1785 (sh)
CpylidMo$(CO)_3$	1904 s,	1808 vs,	1791 (sh)
CpylidW$(CO)_3$	1890 s,	1790 vs,	1780 (sh)
CpylidMo$(CO)_3\cdot BF_3$[a]	2016 w,	1993 (sh),	1957 s,
	1935 s,	1896 (sh)	
CpylidW$(CO)_3\cdot BF_3$[a]	2014 w,	1987 (sh),	1954 s,
	1934 s,	1884 (sh)	

[a] The strong absorption band due to the asymmetric B–F stretch of coordinated BF_3 was found to underlie the bands in the region 1040–1080 cm^{-1} (see ref. 5). In addition, while the parent Cpylidmetal carbonyls have a medium intensity band at 780–800 cm^{-1} and no band at 820–850 cm^{-1}, the situation is reversed for the adducts. The parent Cpylidmetal carbonyls also have bands in the 600–650 cm^{-1} region, while the adducts display only very weak bands in this region. Both the parent compounds and the adducts have strong bands at 600–650 cm^{-1}, but, as this region is characteristic of metal–ring vibrations, major changes occur upon adduct formation. Lastly, medium intensity bands are displayed in the 450–500 cm^{-1} region by the adducts, but not by the parent Cpylidmetal carbonyls.

One additional possibility (V) should be considered. Although the reaction between BF_3 and the Cpylidmetal tricarbonyls is apparently reversible, a slow irreversible process leading to (V) could occur and not drastically change the titration curve shapes. Based on the elemental analysis results, no other formulations for the products seem likely. A structure similar to (V) was proposed as a possibility for the product of a 1/1 reaction between Cp_2MH_2 (M=Mo, W) and BF_3; however, it was rejected for steric reasons[22].



(IV)



(V)

In order to obtain additional information on the nature of the metal–BF_3 complexes, a number of experiments were carried out. As mentioned previously, washing with THF apparently caused the complexes to dissociate; IR spectra of the washings always showed bands for Cpylidmetal tricarbonyl. The molybdenum complex did not react with NMe_3 in toluene due to its insolubility in this solvent. Reaction between the molybdenum and tungsten complexes and NMe_3 occurred in CH_2Cl_2, but a side-reaction of the amine with the solvent[23] caused complications; IR bands typical of the parent Cpylidmetal tricarbonyls were observed in spectra of the reaction products, but $Me_3N\cdot BF_3$ could not be isolated. Shaking a CH_2Cl_2 solution of the tungsten complex with alumina afforded a 65% recovery of pure $CpylidW(CO)_3$.

An attempt was made to determine the molecular weight of the molybdenum complex in CH_2Cl_2 by an isopiestic method. However, the apparent molecular weight was observed to increase over the period of a week. The first determination gave a weight corresponding to that of $CpylidMo(CO)_3$, and the last was considerably higher than that of the BF_3 complex. Dissociation and/or decomposition apparently occurred during the experiment; IR spectra of the recovered solid showed bands quite similar to those observed for the protonated complex in addition to bands for $CpylidMo(CO)_3$ and other CO-containing material.

A mass spectrum of $CpylidMo(CO)_3\cdot BF_3$ showed only the presence of $CpylidMo(CO)_3$ and its fragment ions. A separate experiment indicated that the complex did not lose BF_3 on heating to 160° *in vacuo*. Therefore, it seems likely that, if the solid is indeed the BF_3 complex, the borane is lost as a neutral fragment on electron impact. As an example of the ready loss of ligands as neutral fragments, it was found that the fragment ions corresponding to loss of one or two CO ligands from $CpylidMo(CO)_3$ amounted to only a few percent of the base peak; the base peak was the ion corresponding to loss of all three CO ligands. While this result does not rule out (V), it does make it seem less likely.

The ^{11}B NMR spectra of the pure molybdenum- and tungsten–BF_3 complexes in CH_2Cl_2 showed only a single resonance line at about 1 ppm upfield from $Et_2O\cdot BF_3$. Since we would expect structure (V) to exhibit two resonance lines, this result is more conclusive evidence against (V). Tungsten–boron spin-coupling was not observed; even though saturated solutions were used, the signal-to-noise ratio was too low to allow for the unambiguous observation of the expected satellite lines.

The proton NMR spectrum of a freshly prepared sample of CpylidMo(CO)$_3$ and excess BF$_3$ in CH$_2$Cl$_2$ gave definitive evidence that an additional reaction occurred in solution. A resonance line for Mo–H$^+$ was observed at τ 14.85; the intensity of the line was about 0.2 relative to the 15 phenyl protons. Since every precaution was taken to ensure that the solvent was dry and the BF$_3$ was free of HF, it was thought that the solvent was the source of the proton. There is some precedence for a reaction of this type; Johnson and Shriver reported that CpMo(CO)$_3$H was isolated in small amounts from the reaction of CpMo(CO)$_3^-$ with BF$_3$ in CH$_2$Cl$_2$[22]. Of greater interest, however, is the fact that the high field line did not persist; after the sample had stood at room temperature for about 5 days the line was no longer observed*. Furthermore, the NMR spectra of the purified complexes did not exhibit this high field line.

Based on the information outlined above, it seems reasonable to conclude that, although the system is complicated by a solvent deprotonation reaction, the main reaction between the Cpylidmetal tricarbonyls and BF$_3$ involves the formation of a 1/1 acid–base adduct of the type depicted by structure (IV).

The protonation experiments suggested that the Lewis basicity of the Group VIB metals in the Cpylidmetal tricarbonyls increases in the order Cr < Mo < W. The tensimetric curves also indicate this trend. Although at least a 1/1 reaction was observed for all three compounds at −78°, the equilibrium constants for the reactions at 0° increased with increasing metal atomic weight. If it is assumed that the equilibrium constants reflect enthalpy changes (this requires the reasonable assumption that the entropy changes for all three reactions are nearly equal), the Lewis basicity of the metals *in these compounds* increases in the same order. This conclusion is, of course, made less certain by the presence of the solvent deprotonation reaction previously described. However, qualitative observations also suggest the same order of basicity. Judging from the intensity of the ν(CO) bands for starting material and product, very little product was formed in the CpylidCr(CO)$_3$/BF$_3$ reaction. However, the ν(CO) bands for CpylidW(CO)$_3$ were barely visible after adding BF$_3$. The intensities of the ν(CO) bands for the product and parent compounds were about equal in the molybdenum case.

When Powell and Nöth reacted RhCl(CO)[P(C$_6$H$_5$)$_3$] with BCl$_3$ and BBr$_3$, stable complexes resulted[24]. It had been previously reported that this same rhodium complex would not form an adduct with BF$_3$[25]. This result was not unexpected, since the accepted order of Lewis acid strengths of the boron trihalides is BF$_3$ < BCl$_3$ < BBr$_3$. We have also experienced an apparent increase in adduct stability in the case of BCl$_3$. Tensimetric titrations of CpylidCr(CO)$_3$ and CpylidMo(CO)$_3$ with BCl$_3$ indicated that both metal compounds reacted in a 1/1 ratio with this borane at 0°. On the other hand, we observed little or no interaction between diborane and CpylidMo(CO)$_3$, even at −78°. If it is assumed that BF$_3$ and BCl$_3$ are hard acids and BH$_3$ is a soft acid as suggested by Pearson[26], our experimental results imply that the Cpylidmetal tricarbonyls are hard bases. This is in agreement with Shriver's conclusion that

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* In this connection, it should be noted that a sample of CpylidMo(CO)$_3$·BF$_3$ was prepared by allowing the reactants (and CH$_2$Cl$_2$) to stand in a sealed tube at room temperature for one week. Although the yield of product was apparently higher, the product was identical in every respect with that obtained from the tensimetric experiments.

the di-π-cyclopentadienylmetal dihydrides of molybdenum and tungsten are hard bases toward BF_3[22].

The addition of two molecules of a borane to a transition metal compound has been reported by Shriver[27] and Parshall[6]. Shriver did not specify the location of the second BF_3 except to say that it was probably not attached to the iridium atom in $IrCl(CO)(PPh_3)_2$. However, Parshall suggested that a second BH_3 added to $[Re(CO)_5 \cdot BH_3]^-$ by coordination to the first BH_3 through a B---H---B bridge. The $-78°$ titration curve for the tungsten compound indicates a reaction with more than one BF_3. Although the metal may potentially coordinate to two BF_3 molecules, it seems more reasonable to propose that the second BF_3 coordinates to the first through a B---F---B bridge. Brown has reported several examples of complexes which appear to exhibit such bonding[28]. Furthermore, single fluorine bridges are known to exist in some aluminum compounds[29].

EXPERIMENTAL

Materials and general procedures

Except as noted, the metal carbonyls, triphenylphosphine, and other reagents were used as received. Reagent grade CH_2Cl_2 was distilled from P_2O_5 and stored over molecular sieves in an evacuated bulb. The boron trihalides (Matheson) were purified by trap-to-trap distillation in a high vacuum line: BF_3, v.p. = 303 mm (lit.[30] = 301 mm) at $-112°$; BCl_3, v.p. = 476 mm (lit.[30] = 476 mm) at 0°.

Air sensitive volatile materials were handled in a preparative high vacuum line equipped with mercury float valves[30]. Kel-F grease was used on all joints through which boron trihalides passed. Recrystallization of the products of the Cpylidmetal tricarbonyl/BF_3 reactions, preparation of solutions for infrared work, and thin layer chromatography were done in a Vac-Atmosphere HE-43 drybox; the box was filled with dry N_2 which was circulated through a series of drying and deoxygenating columns[31].

Preparations of metal carbonyl complexes were always carried out in a nitrogen atmosphere. Although the Cpylidmetal tricarbonyls have been reported previously[32], their preparations were not given in detail; therefore, they will be described below.

Analyses were done by Galbraith Laboratories, Inc., and are summarized in Table 3. The mass spectra of the complexes were observed with an AEI-MS-902; the direct inlet system held at 180° was used.

Preparation of starting materials

1. $(C_6H_5)_3PC_5H_4$. Triphenylphosphonium cyclopentadienylide was prepared according to the procedure given by Ramirez and Levy[33].

2. $(C_6H_5)_3PC_5H_4Cr(CO)_3$ and $(C_6H_5)_3PC_5H_4Mo(CO)_3$. Both of these compounds were prepared in 60–80% yields by allowing approximately 2 mmoles of Cpylid to react with the appropriate metal hexacarbonyl (5–6 mmoles) in 60–100 ml of refluxing diglyme. After about 2 h of reflux, the solution was red in the case of the Cr compound and yellow-black in the case of the Mo compound. The reaction mixtures were then cooled to room temperature and filtered. The residue was discarded, and water or hexane was added to the filtrate until the crude yellow product was completely

TABLE 3

ANALYTICAL DATA FOR TRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE DERIVATIVES

Compound	Block formula	Yield (%)	M.p. (°C)[a]	Analyses found (calcd.) (%) C	H	P
Cpylid	$C_{23}H_{19}P$	30–50	238–241	84.75 (85.62)	5.76 (5.87)	9.70 (9.49)
$CpylidCr(CO)_3$	$C_{26}H_{19}CrO_3P$	73	256–258 dec	67.53 (67.52)	4.24 (4.14)	6.88 (6.69)
$CpylidMo(CO)_3$	$C_{26}H_{19}MoO_3P$	61	274–276 dec	61.50 (61.66)	3.69 (3.78)	6.24 (6.11)
$CpylidW(CO)_3$	$C_{26}H_{19}O_3PW$	73	266–268 dec	49.74 (52.54)	3.12 (3.22)	5.11 (5.21)
$CpylidMo(CO)_3 \cdot BF_3$	$C_{26}H_{19}BF_3MoO_3P$		173, dec	54.11 54.38 (54.38)	3.13 3.40 (3.34)	5.21[b] [c] (5.39)
$CpylidW(CO)_3 \cdot BF_3$	$C_{26}H_{19}BF_3O_3PW$		151–154 dec	46.90 (47.16)	2.77 (2.89)	4.72 (4.67)

[a] Sealed capillary. [b] Purified by recrystallizing from CH_2Cl_2/toluene. [c] Purified by washing crude product with THF; average of duplicate analysis.

precipitated. The crude products were recrystallized from $CHCl_3$/petroleum ether to give bright yellow $CpylidCr(CO)_3$ or golden yellow $CpylidMo(CO)_3$.

3. $(C_6H_5)_3PC_5H_4W(CO)_3$. An attempt was made to prepare $CpylidW(CO)_3$ by the same procedure used for the Cr and Mo analogs; however, little or no product could be isolated. King has found $(CN_3CN)_3W(CO)_3$ to be a very reactive compound which may be used as a starting material in the preparation of organo$W(CO)_3$ compounds[34]. Hence, Cpylid was reacted with $(CH_3CN)_3W(CO)_3$ in an attempt to prepare $CpylidW(CO)_3$.

Tris(acetonitrile)tungsten tricarbonyl was prepared by refluxing an acetonitrile/$W(CO)_6$ solution for 40 h. Solvent was then removed by vacuum distillation. The green-yellow product, crude $(CH_3CN)_3W(CO)_3$, was used without further purification.

A magnetically-stirred diglyme solution of Cpylid and $(CH_3CN)_3W(CO)_3$ was heated to 110° for 3 h. The reaction mixture was then cooled to room temperature and the solvent removed by vacuum distillation. Chloroform was added to the yellow-black residue, and this solution was passed down a 9 x 2 cm alumina column maintained under a nitrogen atmosphere. The first fraction of the column was a bright yellow solution of $CpylidW(CO)_3$. After removing the solvent, the yellow-orange solid was recrystallized from $CHCl_3$/petroleum ether to give bright yellow $CpylidW(CO)_3$.

IR and NMR spectra

IR spectra were run on a Perkin–Elmer 337 or 457, the latter being used for all solution work. Spectra of the Cpylidmetal tricarbonyls were obtained in $CHCl_3$ using KBr cells, and those in trifluoroacetic acid were done in Irtran-2 cells.

Proton NMR spectra were obtained on a Varian A-60 spectrometer; the side-band technique was used for calibration. The protonated Cpylidmetal tricarbonyls were prepared by placing CpylidM$(CO)_3$ in an NMR tube attached to the vacuum line; TFA and TMS were then distilled into the tube before it was sealed off. The resulting solutions were highly colored: Cr, yellow; Mo, deep red; W, deep blue. Solutions of CpylidM$(CO)_3$ (M = Mo, W) in CH_2Cl_2 containing a 2/1 excess of BF_3 were prepared directly in NMR tubes attached to the vacuum line; these samples were kept at $-196°$ until needed. ^{11}B NMR spectra were done on a Varian HA-100 spectrometer and were referenced to external $Et_2O \cdot BF_3$.

Tensimetric titration of the Cpylidmetal tricarbonyls with boranes

Approximately one mmole of CpylidM$(CO)_3$ and a Teflon-covered stirring bar were placed in a flask which was then attached to the vacuum line. After distilling in about 10 cc of dry CH_2Cl_2 and measuring the vapor pressure of the solution at 0° and $-78°$, successive small increments (0.1 to 0.3 mmole) of BF_3, BCl_3, or B_2H_6 were distilled into the solution. The titration curves shown in Figs. 2 and 3 are representative of two runs using CpylidCr$(CO)_3$, eight runs using CpylidMo$(CO)_3$, and four runs with CpylidW$(CO)_3$.

While the Cpylidmetal tricarbonyls were not entirely soluble in the amount of solvents used, the reaction products were completely soluble. The colors of the solutions were: CpylidCr$(CO)_3/BF_3$, yellow; CpylidMo$(CO)_3/BF_3$ and CpylidW$(CO)_3/BF_3$, deep red.

Isolation of the CpylidM$(CO)_3 \cdot BF_3$ complexes

The solid products from the BF_3 tensimetric titrations were purified by quickly recrystallizing from CH_2Cl_2/toluene or by washing with dry THF. The purified materials were deep red and air-stable for many months. IR data for the purified solids are given in Table 2 and analytical results in Table 3. Products from BCl_3 reactions decomposed on attempting to purify them.

Isopiestic molecular weight

A special apparatus (Fig. 4) was designed to determine the molecular weight of air-sensitive materials at room temperature or higher by the isothermal distillation or isopiestic technique[30]. A sample of the standard (azobenzene) was introduced through side-arm A, and the unknown was introduced through B; these side-arms were then sealed off. After distilling in the solvent (CH_2Cl_2) from the vacuum line, the apparatus was immersed up to the needle valve (Delmar–Urry) in a constant temperature bath at 30°. After equilibration, the float valve was closed and the solvent in the "unknown" side was distilled from the apparatus and into a weighing bulb on the vacuum line. The weight of solvent in the "standard" side was determined in the same manner. The method gave an accuracy of ±4% when tested with Cpylid as the unknown.

When an attempt was made to determine the molecular weight of CpylidMo$(CO)_3 \cdot BF_3$, 494 g/mole was found after two days of equilibration at 30°. The solvent was distilled back into the apparatus and re-equilibrated for three days; 613 g/mole was found. A third determination by the same procedure gave 666 g/mole. The calculated molecular weights for CpylidMo$(CO)_3$ and its BF_3 complex are 506 and 574 g/mole, respectively.

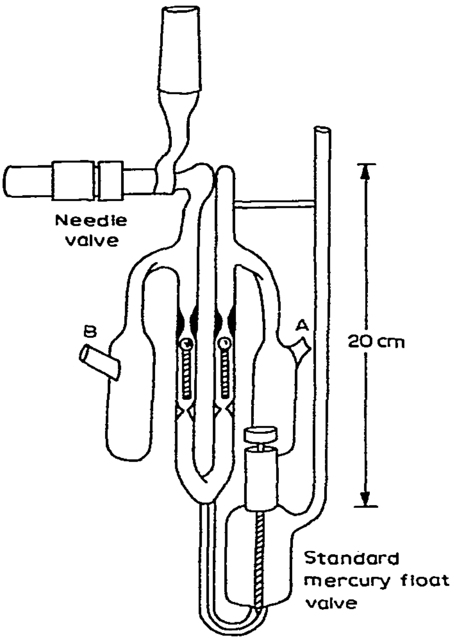

Fig. 4. Apparatus for the determination of the molecular weight of an air-sensitive material at temperatures higher than room temperature by the isothermal distillation technique. A ¾ view of the apparatus is shown.

Reactions with alumina and trimethylamine

The alumina reaction was run in an all-glass *zweikügel*, an apparatus which is essentially an H-tube, the arms of which can be opened to the vacuum line through glass break-seals. Approximately 2 g of alumina and 0.283 g of CpylidW(CO)$_3$·BF$_3$ were placed in one arm of the *zweikügel*. After distilling in about 5 cc of CH_2Cl_2 from the vacuum line, the apparatus was sealed off. The solution was initially deep red, but changed to yellow over about a three day period. The solution was decanted from the alumina into the other arm of the *zweikügel*; after washing the alumina several times with CH_2Cl_2, the *zweikügel* was attached to the vacuum line and the solvent removed. 64.5% of the theoretical amount of CpylidW(CO)$_3$ was recovered.

Reactions with NMe$_3$ were done by condensing solvent and an excess of the amine into a flask or tube containing one of the BF$_3$ complexes. After the reaction had apparently gone to completion, the amine and solvent were removed at 0°; the solid residue was heated *in vacuo* in an attempt to sublime off any Me$_3$N·BF$_3$ which may have been formed.

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