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Ligand Influence on the Electronic Properties of Some Bis(tertiary phosphine)-Substituted Chromium and Molybdenum Carbonyls: Cyclic Voltammetry and Infrared Spectroscopy of $M(CO)_4R_2PCH_2CH_2PR_2$

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Received July 19, 1983

The bidentate phosphines $R_2PCH_2CH_2PR_2$ (R = F, Cl, C_6F_5, CH_3O, C_6H_5, CH_3, and c-C_6H_{11}) and their respective chromium and molybdenum complexes were synthesized to provide a wide range of electronic effects at the metal center. Cyclic voltammetry and infrared spectroscopy were used to determine relative charge density at the metal center. As determined by cyclic voltammetry the π-acceptor strength of the ligands $R_2PCH_2CH_2PR_2$ decreases in the order R = F > Cl > C_6F_5 > CH_3O > C_6H_5 > CH_3 > c-C_6H_{11}. A linear correlation between $k(CO)_{trans}$ and the value $E_{1/2} = (E_a + E_c)/2$ was found for the series $M(CO)_6$ and $M(CO)_4R_2PCH_2CH_2PR_2$ (where M = Cr or Mo and R = F, Cl, C_6F_5, CH_3O, and C_6H_5). The complexes containing the ligands $(CH_3)_2PCH_2CH_2P(CH_3)_2$ and $(c\text{-}C_6H_{11})_2PCH_2CH_2P(c\text{-}C_6H_{11})_2$ do not fall on this line but lie below it. The existence of these two groups of phosphines is argued to reflect the difference in the π-acceptor capabilities of the ligands.

The electronic effects of ligands on the properties of the associated transition metal can, in principle, be probed in a variety of ways. Emerging as a particularly useful tool is cyclic voltammetry.[1-7] Electrochemical measurements are very sensitive to small changes in the electron distribution about the metal center, and they offer the advantages over many other tools of applicability to complexes in solution (similar to the environment of the complex in most chemical processes), they are readily available to many laboratories, and they are relatively easy to use. Although the experimental results of cyclic voltammetry are a function of the solvent and reference electrode used, it has been shown that the heterogeneous redox reactions taking place at electrode surfaces and the homogeneous reactions taking place in solution are governed by similar factors.[1,2,8-10]

Under favorable conditions electrochemical measurements can provide information about the relative energies of the HOMO's and/or LUMO's of a series of related compounds. The oxidation potentials for a series of complexes $Mn(CO)_{6-x}(CNPh)_x^+$ x = 1-6, have been shown to be linearly related to the HOMO energies calculated by approximate molecular orbital methods.[3] Assuming this holds for other series, then the change in redox potential represents the change in energy of the HOMO. Oxidation potentials have also been correlated with changes in vibrational frequencies[4] and chemical reactivities.[5]

For these reasons we chose to apply cyclic voltammetry to assess the range of effects that can be generated by varying the substituents on the phosphine ligands in a series of similar compounds and to analyze those effects. We chose the series of compounds $M(CO)_4L$, where L is a bidentate phosphine ligand of the type $R_2PCH_2CH_2PR_2$ and M = Cr, Mo. There were several reasons for these choices. First, a variety of bis(tertiary phosphines) of this kind was known or could potentially be prepared. The bidentate ligands help to minimize the extent of ligand dissociation and the complications arising from it. The compounds were expected to exhibit a limited range of geometry at the metal center: the ethylene bridge physically limits the range of P-M-P angles, the presence of linear CO ligands in adjacent positions minimizes steric interaction with the R groups, and the presence of only two bulky groups on phosphorus in some instances, rather than three, helps avoid excessive steric interaction.[11] (Cotton and coworkers[12] found only a small deviation in P-M-P angle between $(CO)_4Mo(PMePh_2)_2$ and $(CO)_4Mo(PMe_2Ph)_2$, for example.) The group 6B metal carbonyl derivatives were chosen because they provide a complementary probe of metal-ligand bonding in the CO ligands,[13] the near-octahedral geometry of the phosphine derivatives provides a maximum separation of σ and π bonding factors, the low-spin d^6 configuration simplifies interpretation of the experiments,[3] and the parent hexacarbonyls had been shown to exhibit reversible electrochemistry.[14,15]

Experimental Section

Materials. All solvents were dried by standard methods.[16] Reactions were carried out under nitrogen, and inert-atmosphere techniques were used in handling the reactants and products.[17] The compounds 1,2-bis(dichlorophosphino)ethane (dcpe), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Strem Chemicals, Inc., and were used as received. The group 6B metal carbonyls were purchased from Strem Chemicals, Inc., and were sublimed before use. Tetrabutylammonium perchlorate was purchased from Eastman Kodak, recrystallized from chloroform at -20 °C, and then dried overnight at 100-110 °C in a vacuum oven before use. The following ligands were synthesized by literature methods: 1,2-bis(dicyclohexylphosphino)ethane (dcype),[18] 1,2-bis(dimethoxyphosphino)ethane (dmepe),[19] and 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (dpfpe).[20] The final ligand used was prepared as follows:

1,2-Bis(difluorophosphino)ethane (dfpe). Dry benzene (40 mL) and 18-crown-6 (5.0 g, 18 mmol) (18 crown-6 is the cyclic polyether

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1,4,7,10,13,16-hexaoxacyclooctadecane) were added to a dry 100-mL round-bottom flask. The flask was stoppered and stirred with a magnetic stirrer to effect solution of the 18-crown-6. Anhydrous potassium fluoride (8.5 g, 146 mmol) was then added. The apparatus was fitted with a reflux condenser and attached to a vacuum line. The system was degassed three times with use of a freeze–thaw process and then stirred an additional $^1/_2$ h. 1,2-Bis(dichlorophosphino)ethane (4 g, 7.3 mmol) was then transferred, via the vacuum line, to the potassium fluoride reagent. The mixture was heated to 50 °C, stirred for 24 h, and then allowed to cool, and the liquids were vacuum distilled through traps at −63, −84, and −196 °C. The product in the −84 °C trap was redistilled in the same way. Pure $F_2PCH_2CH_2PF_2$, 47% yield from $Cl_2PCH_2CH_2PCl_2$, was retained in the −84 °C trap. The product was identified by infrared and NMR spectroscopy.[21]

The following were prepared by literature methods: $M(CO)_4NBD$[22] (NBD = norbornadiene bicyclo[2.2.1]hepta-2,5-diene), $M(CO)_4dppe$,[23] $M(CO)_4dmpe$,[24] and $M(CO)_4dfpe$[25] (M = Cr, Mo). $M(CO)_4dcype$, M = Cr, Mo, was prepared with use of the sodium borohydride catalyzed method of Chatt and co-workers.[26]

$Cl_2PCH_2CH_2PCl_2M(CO)_4$, M = Cr, Mo. $Cr(CO)_4NBD$ (0.75 g, 2.9 mmol) and dcpe (0.75 g, 3.2 mmol) in 25 mL of dry hexane were refluxed under nitrogen for 18 h. The solution was allowed to cool and the solvent removed under vacuum. Pumping was continued overnight to remove unreacted $Cr(CO)_4NBD$. The remaining crystals were dissolved in warm hexane and applied to a Florisil column. Due to the low solubility of $M(CO)_4dcpe$ (M = Cr, Mo) in hexane (and other solvents tried), only 5–10 mg of these compounds could be recovered in a single run. Elutions with hexane proceeded until the yellow band corresponding to $Cr(CO)_4NBD$ began to elute. The solvent from the colorless eluent was removed under vacuum to give 0.51 g, 44% yield, of white crystalline $Cr(CO)_4dcpe$. Anal. Calcd: C, 18.21; H, 1.02; P, 15.65. Found: C, 18.23; H, 1.04; P, 15.61. The molybdenum analogue was prepared by the same method to give 0.76 g, 52%, of white crystalline $Mo(CO)_4dcpe$. Anal. Calcd: C, 16.39; H, 0.917; P, 14.09. Found: C, 16.41; H, 0.919; P, 14.14.

(1,2-Bis(pentafluorophenyl)phosphino)ethane)tetracarbonylchromium(0) and -molybdenum(0). $Cr(CO)_4NBD$ (0.25 g, 0.94 mmol) and dpfpe (0.75 g, 0.99 mmol) in 75 mL of acetone were refluxed under nitrogen for 72 h. The solution was allowed to cool and the solvent removed under vacuum. The resulting crystals were transferred to a sublimation apparatus, and unreacted $Cr(CO)_4NBD$ was removed at 90 °C (0.1 mm). Recrystallization of the residue from hot acetone gave 0.41 g, 46%, of $Cr(CO)_4dpfpe$. Anal. Calcd: C, 39.07; H, 0.437; P, 6.72. Found. C, 39.10; H, 0.440; P, 6.77. The molybdenum analogue was prepared in the same manner to give 0.46 g, 32%, of $Mo(CO)_4dpfpe$. Anal. Calcd: C, 37.29; P, 6.42. Found: C, 37.31; P, 6.44.

Experimental Procedures. Infrared spectra were obtained with a Perkin-Elmer 599 spectrometer. Solution spectra were obtained in carbon disulfide in microcavity cells. For air-sensitive samples the solvent was degassed before use and the sample introduced to the cell under an inert atmosphere. Values reported in the text are correct to ±1 cm^{-1} (polystyrene reference).

Electrochemical Measurements. When not in use the supporting electrolyte, recrystallized TBAP, was stored in a desiccator. The two solvents used were acetonitrile and dichloromethane. Acetonitrile was purified by two distillations from potassium permanganate and a final distillation from anhydrous potassium carbonate. Dichloromethane was purified by two distillations from phosphorus pentoxide and a final distillation from potassium carbonate. The cyclic voltammograms were obtained with a PARC 175/174A system. A three-electrode cell consisting of a glassy-carbon working electrode, a platinum-flag counterelectrode, and a saturated aqueous calomel reference electrode was used. An initial background scan was run to check the purity of the reagents and to establish the solvent anodic potential range. The cyclic voltammetric scans were started at 0 V and increased to an anodic voltage beyond the oxidation wave. The potential was then reversed and the scan continued until a potential of −0.5 V was reached. The potential was reversed again and halted at the initial value of 0 V. In order to minimize the effect that changing the scan rate has on quasi-reversible systems, the scan rate used in all experiments was 500 mV/s.

Table I. Infrared Carbonyl Stretching Frequencies[a] and Force Constants[b] for $M(CO)_4R_2PCH_2CH_2PR_2$ Compounds (M = Cr, Mo)

R	A_1^1	A_1^2	B_1	B_2	k_1	k_2
			Cr			
F	2056	1998	1982	1970	15.94	16.39
Cl	2050	1995	1980	1966	15.87	16.30
C_6F_5	2039	1969	1940	1913	15.23	15.83
CH_3O	2025	1952	1935	1912	15.11	15.71
c	2051	1929	1935	1888	14.89	15.86
C_6H_5	2009	1914	1899	1877	14.75	15.32
CH_3	2009	1921	1900	1894	14.83	15.30
C_6H_{11} [d]	2002	1912	1890	1886	14.71	15.17
			Mo			
F	2074	2005	1991	1973	16.04	16.57
Cl	2061	2002	1985	1972	15.98	16.43
C_6F_5	2049	1973	1948	1917	15.25	15.99
CH_3O	2033	1965	1941	1916	15.18	15.82
c	2057	1927	1945	1887	14.90	15.98
C_6H_5	2020	1919	1907	1881	14.87	15.48
CH_3	2020	1929	1909	1903	14.98	15.46
C_6H_{11}	2016	1922	1896	1888	14.78	15.32

[a] In cm^{-1} in carbon disulfide. [b] In mdynes/Å. [c] $M(CO)_4$ fragment in a methane matrix.[44] [d] C_6H_{11} = cyclohexyl.

Results and Discussion

A new synthetic procedure was developed for the preparation of $F_2PCH_2CH_2PF_2$. 1,2-Bis(difluorophosphino)ethane (dfpe) was first synthesized by means of a photoreaction[21] that required a five-step procedure and resulted in relatively poor yields. The new method requires only a single step utilizing a phase-transfer catalyst. It has been shown[27] that potassium fluoride can be solubilized in acetonitrile or benzene to become a strong nucleophile, which gives rise to facile substitution of fluoride for other halides in a variety of compounds. The reaction of anhydrous potassium fluoride and dcpe in the presence of 18-crown-6 polyether in benzene results in the conversion of dcpe to dfpe in yields as high as 47%. Somewhat surprising is our near-complete lack of success in effecting this conversion by using the preferred method for fluorination of e.g. Cl_2PNMe_2, i.e. NaF in sulfolane.[28]

Four new phosphine-substituted group 6B metal carbonyls, $M(CO)_4dcpe$ and $M(CO)_4dpfpe$, M = Cr, Mo, were also synthesized in the course of this research. All four compounds are physically similar to others of the class except for their solubilities, especially the complexes of dpfpe and dcpe, both of which have low solubility in hydrocarbon solvents. Comparison of both the A_1^1 stretching frequencies and the corresponding force constants (calculated by the method suggested by Brisdon and Griffin[29]) (Table I) show that the two ligands dcpe and dpfpe are relatively strong π-acceptor ligands as expected. On the basis of the calculated force constants, the order of π-acceptor strength for the ligands used in this study is, for $R_2PCH_2CH_2PR_2$ ligands:

$$R = F > Cl > C_6F_5 > CH_3O > CH_3 > C_6H_5 > C_6H_{11}$$

Except for CH_3 this order follows the electronegativity of the substituent atoms on phosphorus.

Cyclic Voltammetry. The results of the electrochemical measurements are summarized in Table II. The $E_{1/2}$ values

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Table II. Cyclic Voltammetric Data[b] for $M(CO)_6$ and $M(CO)_4R_2PCH_2CH_2PR_2$ Complexes in Dichloromethane and Acetonitrile (M = Cr, Mo)

		Cr			Mo		
solvent	R[a]	E_a	E_c	$E_{1/2}$	E_a	E_c	$E_{1/2}$
CH_2Cl_2	$M(CO)_6$						
	F						
	Cl						
	C_6F_5	1.235	0.860	1.05	1.46	1.10	1.28
	CH_3O	1.15	0.840	0.995	1.38	1.04	1.21
	C_6H_5	1.025	0.690	0.86	1.24	0.86	1.05
	CH_3	1.59	0.325	0.46	0.710	0.470	0.590
	C_6H_{11}[d]	0.560	0.260	0.41	0.670	0.390	0.530
CH_3CN	$M(CO)_6$	1.49	1.32	1.41	1.65		
	F	1.32	1.18	1.25	1.37		
	Cl	1.24	1.09	1.17	1.50		
	C_6F_5	1.01	0.87	0.94	1.23		
	CH_3O	0.96	0.82	0.89	1.18		
	C_6H_5	0.795	0.675	0.735	0.985		
	CH_3	0.35	0.19	0.27	0.46		
	C_6H_{11}	0.265	0.15	0.21	0.36		

[a] Except for the parent carbonyl. [b] In volts vs. SCE, glassy-carbon working electrode, tetrabutylammonium perchlorate supporting electrolyte. [c] $E_{1/2} = (E_a + E_c)/2$. [d] C_6H_{11} = cyclohexyl.

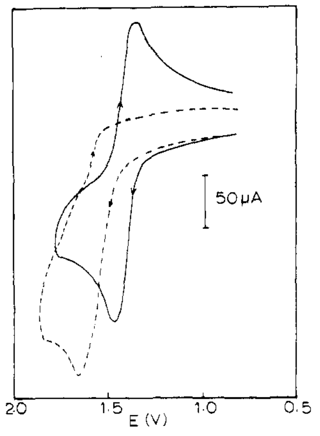

Figure 1. Cyclic voltammograms of $Cr(CO)_6$ (—) and $Mo(CO)_6$ (---) in acetonitrile at a glassy-carbon electrode (reference electrode SCE, TBAP supporting electrolyte, 500 mV/s scan rate).

reported correspond to the mean of the peak potentials of the anodic and cathodic waves, $E_{1/2} = (E_{p,a} + E_{p,c})/2$, for the process $M(CO)_4L \rightleftarrows M(CO)_4L^+ + e^-$. Peak separations greater than 59 mV suggest that the electrode reactions are, at best, quasi-reversible.[30] It is well-known, however, that high solution resistance in nonaqueous solvents can lead to large peak separations which can vary from solvent to solvent and with the reference electrode used.[31,32] For comparison ferrocene[31,33] was examined under the same experimental conditions in both solvents and was found to give ΔE_p = 80–95 mV in CH_3CN and ΔE_p = 100–120 mV in CH_2Cl_2 solution at a glassy-carbon working electrode at a scan rate of 500 mV/s. ($E_{1/2}$ for ferrocene in CH_2Cl_2 was observed at +0.495 V).

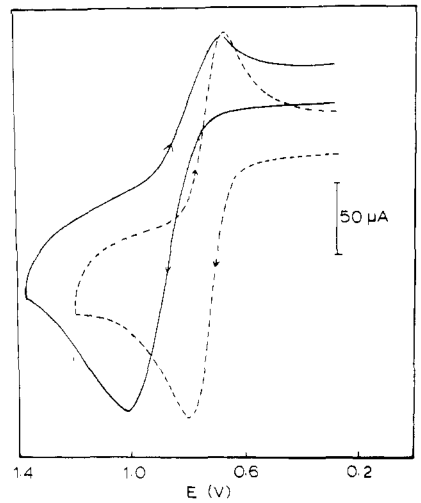

Figure 2. Cyclic voltammograms of $Cr(CO)_4$dppe in CH_2Cl_2 (—) and in CH_3CN (---) at a glassy-carbon electrode (reference electrode SCE, TBAP supporting electrolyte, 500 mV/s scan rate).

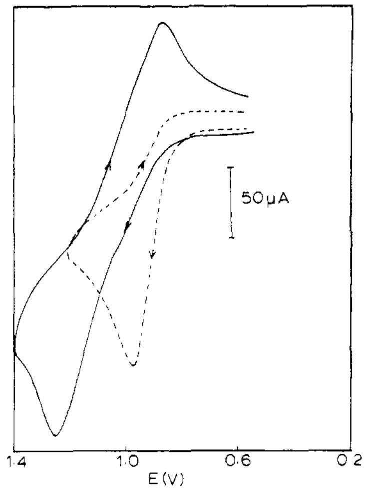

Figure 3. Cyclic voltammograms of $Mo(CO)_4$dppe in CH_2Cl_2 (—) and in CH_3CN (---) at a glassy-carbon electrode (reference electrode SCE, TBAP supporting electrolyte, 500 mV/s scan rate).

Both solvents used displayed advantages and disadvantages to our purpose. These are illustrated by the voltammograms of $Cr(CO)_6$, $Mo(CO)_6$, and $Cr(CO)_4$dppe and $Mo(CO)_4$dppe (Figures 1–3). In acetonitrile $Cr(CO)_6$ displayed electrochemical quasi-reversible behavior with a peak separation of 170 mV and an i_a/i_c ratio of about 1:1. $Mo(CO)_6$ showed no reverse (reduction) wave in acetonitrile (nor did $W(CO)_6$), presumably because of the greater ease of its assuming seven-coordination in the coordinating solvent. None of the three hexacarbonyls gave an oxidation wave in dichloromethane below the solvent decomposition wave >1.6 V. Essenmacher and Treichel[6] noted previously that the oxidation potentials of hexakis(aryl isocyanide)chromium(0) complexes diminish from dichloromethane to acetonitrile, and we conclude that the hexacarbonyl waves are obscured by solvent oxidation. The $M(CO)_4$dppe data support these assumptions. Electrochemical quasi-reversibility was observed for both Cr and Mo complexes in dichloromethane while only the anodic wave was observed for the Mo complex in acetonitrile. From the greatly diminished return wave for $Cr(CO)_4$dppe in CH_2Cl_2 (Figure 2) it is evident that the oxidized species is unstable in dichloromethane and undergoes decomposition or chemical reaction with the solvent. In acetonitrile, however, the return wave is much more prominent, perhaps due to the higher dielectric constant of acetonitrile as compared to dichloromethane resulting in greater stabilization of the electrochemically generated cation. Also, in agreement with the observation of Essenmacher and Treichel,[6] we note a larger peak to peak separation in dichloromethane than in acetonitrile, an average for the phosphine complexes of 320 mV in CH_2Cl_2 vs 145 mV

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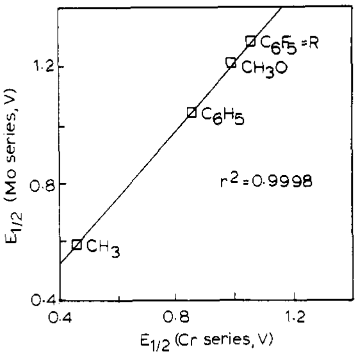

Figure 4. Correlation between $E_{1/2} = (E_a + E_c)/2$ for the series $M(CO)_4R_2PCH_2CH_2PR_2$, M = Cr, Mo.

in CH_3CN. These differences are not unexpected.[32,34] The stronger π-acid ligands (e.g. pfpe), like CO, give complexes apparently oxidizing beyond the solvent limit in dichloromethane, but anodic waves, at least, are observed in acetonitrile in all cases.

As seen in Table II, the total range in $E_{1/2}$ for the disubstituted group 6B tetracarbonyl is about 1.0 V for both the molybdenum and the chromium series. Several aspects of these results are noteworthy. As one goes from Cr to Mo, there is an increase in the value of $E_{1/2}$. This is consistent with previous data for similar series.[6] The results also indicate that there is a correlation between the donor/acceptor character of the ligands and the $E_{1/2}$ values of the complexes. The phosphorus ligands might affect the HOMO energy of the complex in two ways. First, the energy of the π-type HOMO might be modified indirectly by an increase in electron density on the metal due to the Lewis base σ-donation by the phosphorus ligand. In concert with this effect is the more direct withdrawal of electron density from the metal through π backbonding. If the ligand is a good net acceptor of electron density, there should result a lowering of the HOMO energy and a corresponding increase in the oxidation potential of the complex. The ability of the phosphorus ligands to remove charge from the metal follows qualitatively the order of electronegativity of the substituents on the phosphorus donor atom as expected, i.e. $F > Cl > C_6F_5 > C_6H_5 > CH_3 > C_6H_{11}$.

In Figure 4 a plot of the $E_{1/2}$ values of the chromium complexes vs. the $E_{1/2}$ values of the corresponding molybdenum complexes is shown. The linear correlation for the two sets of data is very good ($r^2 = 0.9998$). The least-squares best fit is given by $E_{1/2}(Mo) = 1.17[E_{1/2}(Cr)] + 0.052$. The slope of 1.17 indicates that for the same ligand there is more charge removed from the metal when the metal is molybdenum than when the metal is chromium. This is consistent with the greater extension of the 4d orbitals of the second-row metals compared to the 3d orbitals of the first-row meatals resulting in greater overlap of the metal orbitals with the phosphorus 3d orbital. The phosphines can thus reduce electron density more effectively on Mo than on Cr. The linearity of the two sets of data also allows one to predict the $E_{1/2}$ value of the analogue when that for a given ligand of either the Mo or Cr tetracarbonyl derivative is known.

There have been many attempts to correlate the redox potentials of a series of compounds with a variety of other parameters. Pickett and Pletcher[35] demonstrated that for a series of $M(CO)_{6-x}L_x^{y+}$ compounds the potential is a function of the number x and the nature of L. Ligands observed were primarily cyanides and isocyanides. Others have plotted redox potential against linear free energy parameters for the ligands.[6]

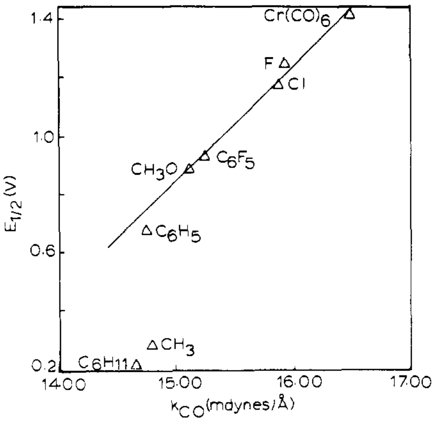

Figure 5. Correlation between $E_{1/2} = (E_a + E_c)/2$ and k_{CO} for $Cr(CO)_6$ and $Cr(CO)_4R_2PCH_2CH_2PR_2$.

Several groups have noted linear relationships between the redox potentials and carbonyl or dinitrogen stretching frequencies.[36-38] In Figure 5 a plot of the redox potentials of the chromium series studies in this research vs. the carbonyl force constants for the same series of compounds is shown. A linear correlation was found for the series $Cr(CO)_6$ and $Cr(CO)_4R_2PCH_2CH_2PR_2$ where R = F, Cl, C_6F_5, CH_3O, and C_6H_5. However, the two compounds where R = CH_3 and C_6H_{11} fall considerably below this line and might constitute a portion of a second line. It is noteworthy that the two compounds which fall below the line contain ligands that would be expected not to π bond extensively to the tetracarbonyl fragment. The ability of the ligands falling on the line to withdraw electron density from the metal results in higher oxidation potentials than for those ligands that are unable to π bond effectively. That $Cr(CO)_6$ lies on the line suggests that the bonding in those ligands is similar to that in carbonyl. The sharp separation of these data into two sets contrasts markedly with the results of Chatt and co-workers[39] and, we believe, reflects the broader range of bonding character in the set of ligands considered here. The range of $E_{1/2}$ values of 1.0 V is near double that previously observed in a similar series. Such a division into two separate sets of phosphine ligands is not, however, without precedent. Lappert, Stelzer, and co-workers[40] found that a plot of the first ionization potentials of free phosphines vs. the A_1 carbonyl stretching frequencies of the respective phosphine-disubstituted molybdenum tetracarbonyl derivatives resulted in three separate lines. It was suggested that the three lines represent the varying π-acceptor abilities for the ligands. The ionization potentials for the monodentate analogous of the bidentate ligands used in this study were plotted against the A_1 carbonyl stretching frequencies of the disubstituted molybdenum tetracarbonyl complexes (data from ref 40).[6] The ionization potential for $CH_3P(C_6H_5)_2$ has not been reported and was estimated by plotting the ionization potentials of the series $(CH_3)_3P$, $(CH_3)_2PC_6H_5$, and $(C_6H_5)_3P$ and interpolating. In agreement with the results obtained from this study, the ligands $(CH_3)PR_2$, R = F, Cl, C_6H_5, fell on the same line and the ligand with R = CH_3 was displaced significantly.

The results of this research indicate that two parameters (at least) are required to adequately describe the bonding

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between the metal and phosphine ligands. It has long been argued that there is synergic interaction between σ-donor and π-acceptor effects, that better donation by the ligand leads to better donation by the metal and enhanced π acceptance by the ligand. The two components of bonding, in other words, are coupled in the phosphines to a degree. The CO stretching frequency or force constant has been argued to provide a comparative scale of inherent π acidities,[41] but it has been effectively argued that these quantities also reflect σ effects,[42] perhaps to a lesser extent. The carbonyl stretch may, in fact, most nearly reflect the effective net charge of the metal center. In the systems studied here, ν_{CO} or the CO stretching force constant increases nearly monotonically with the apparent electronegativities of the phosphorus substituents from cyclohexyl to fluorine. The corresponding increase in $E_{1/2}$ shows, however, the sharp break following methyl described above, suggesting that in these pseudooctahedral d^6 complexes the separation between σ and π effects may be more pronounced in electrochemical measurements than in measurements of the carbonyl stretch. This is consistent with a recent suggestion by Bursten.[7]

Given the trends observed in this report and by Lappert, Stelzer, and coworkers,[40] it seemed reasonable to expect similar behavior for monodentate phosphines in a plot of $E_{1/2}$ vs ν_{CO}. In fact, with use of data obtained for $\mathrm{Cr(CO)_5}$(ligand) by Lloyd et al.,[43] *no* such correlation was observed. The $E_{1/2}$ values of these complexes were also plotted against linear free energy parameters for the phosphines, chromium core electron binding energies, and the electronegativities of the substituents on phosphorus. No correlations were found. At the concentrations used for the cyclic voltammetry scans (5×10^{-4} M), ligand dissociation, much more likely for the monodentates than bidentates, may be a significant factor in this lack of correlation.

Summary

The results of this study demonstrate that bidentate phoshines can be prepared that achieve a very broad range of effects on the electronic properties of transition metals as reflected in oxidation potentials and CO stretching force constants. Together with other recent work they demonstrate that electrochemical methods provide a sensitive technique for the study of bonding in transition-metal carbonyls. The separation into two distinct groups of the bidentate phosphines lends support to the common, but hotly argued, assumption that phosphines do in many instances engage in significant π bonding in complexes of this kind or *at least* that more than simple σ-donor effects must be considered. Perhaps as important, this separation suggests that in some instances (e.g. R = $\mathrm{CH_3}$ or $\mathrm{C_6H_{11}}$) π bonding may *not* be a significant consideration at all.

Acknowledgment. We wish to thank Drs. Brisdon and Griffin for the generous donation of the computer program for the force constants calculation. We also wish to thank Dr. Jack Spence for the use of his electrochemical apparatus (NIH Grant GM08347).

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Oxidation of Isopropylamine and Related Amines Coordinated to Ruthenium. Formation of Monodentate Imine and Alkylideneamido Complexes of Ruthenium

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Received June 9, 1983

The chemical and electrochemical oxidation of $[\mathrm{Ru(tpy)(bpy)(NH_2CHR^1R^2)}]^{2+}$ ($\mathrm{NH_2CHR^1R^2}$ = isopropylamine, cyclohexylamine, or (α-methylbenzyl)amine; tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine) reveals two consecutive two-electron processes. The first oxidation is irreversible and yields the corresponding imine species. The second oxidation produces a complex identified as containing the N-bound alkylideneamide anion. The second process is reversible chemically or electrochemically. The X-ray crystal structure of $[\mathrm{Ru(tpy)(bpy)(NCMe_2)}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$ (the four-electron oxidation product of the complex containing isopropylamine) shows a linear Ru–N–C linkage with a Ru–N bond length of 1.831 (10) Å, indicating multiple bonding. The complex of formula $\mathrm{C_{28}H_{27}N_6Cl_3O_{13}Ru}$ is orthorhombic, space group $Pna2_1$ (No. 33), with cell dimensions a = 22.034 (13) Å, b = 10.689 (6) Å, c = 14.251 (9) Å, and Z = 4.

Introduction

There has been considerable recent interest in the oxidative dehydrogenation of coordinated amines to the corresponding imines or nitriles.[3–7] Many of these studies have involved ruthenium as the metal center, and while the formation of complexes containing the α,α'-diimine moiety has been relatively common,[3,5] complexes containing coordinated simple monodentate imines had not been isolated although their intermediacy had been either observed or inferred in a few cases.[3,4]

We recently communicated[8] aspects of the oxidation of isopropylamine in the complex $[\mathrm{Ru(tpy)(bpy)(NH_2CHMe_2)}]^{2+}$,[9] in which two major processes were observed. Initially, a two-electron oxidation yielded the corre-

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(9) Abbreviations for ligands: bpy = 2,2′-bipyridine; tpy = 2,2′:6′,2″-terpyridine; bpic = 4,4′-dimethyl-2,2′-bipyridine.

0020-1669/84/1323-2336$01.50/0