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Preliminary communication

REACTIONS OF ELECTRON-RICH ORGANOMETALLIC COMPLEXES

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Summary

Various transition metal complexes of the types $C_5H_5FeL_2X$, $C_5H_5Mn(CO)L_2$, and MnL_5X (L = isocyanides, phosphines, phosphites; X = halides, Me, SnX_3) have been prepared. These complexes were found to undergo either facile one electron oxidations, giving isolable 17*e* species, or they can lose X^-, giving intermediates (not isolated) which react either with other added ligands, or with ligands present from complex degradation.

The purpose of this communication is to direct attention to a type of organometallic complex having a relatively electron-rich metal center, and to define various general reactions unique to these species.

Previous work in our group on isocyanide complexes of manganese and chromium [1,2] showed that the ease of oxidation, measured electrochemically as an $E_{1/2}$ value, is substantially dependent on the ligand groups attached to the metal. For example, in the series $[Mn(CO)_{6-n}(CNMe)_n]^+$ the values of $E_{1/2}$ decreased by about 0.4 V on successive carbonyl substitution by the isocyanide. This result can be equated qualitatively with the net donor characteristics (both σ and π) of the ligand; the effect of substitution of a better donor ligand, CNMe, for a poorer one, CO, is to increase the metal electron density, which in turn causes the metal to be more prone to loss of an electron. Theoretical arguments have added some reassurence to this rationale [3].

In attempting to broaden somewhat a framework of reference in this area, we have prepared various metal complexes of isocyanides, phosphines, and of other ligands. Our initial interest was directed to the redox properties of these complexes and to the isolation of products obtainable through one electron oxidation. It may be observed that definite criteria seem to determine whether this is possible [4]. However, as this work developed it became apparent that other typical reactions of these complexes might also be formulated, and our interest broadened to encompass other chemical reactions which might be unique to these systems.

Data on electrochemical oxidations of 19 metal complexes with formulas

TABLE 1

VOLTAMMETRIC AND CHEMICAL OXIDATION DATA

		X	$\frac{1}{2}[E_{p,c}+E_{p,a}]^a$	$\frac{1}{2}[E_{p,c}-E_{p,a}]^c$	Attempted chemical oxidation (see discussion)^d	
			(V)	(V)	$AgPF_6$	$NOPF_6$
(a)	$C_5H_5Fe(diphos)X$	Me	−0.26v	0.270	$[C_5H_5Fe(diphos)Me]PF_6$	
		H	−0.08	0.115	^{e}	
		Cl	0.08	0.055	$[C_5H_5Fe(diphos)Cl]PF_6$	
		$SnMe_3$	0.065	0.121	$[C_5H_5Fe(diphos)SnMe_3]PF_6$	
		Br	0.11	0.065	$[C_5H_5Fe(diphos)Br]PF_6$	
		I	0.15	0.066	$[C_5H_5Fe(diphos)I]PF_6$	
		$SnCl_3$	0.90	0.105		
(b)	$C_5H_5Fe(CO)[P(OPh)_3]I$		0.06	0.057		$[C_5H_5Fe(NO)P(OPh)_3I]PF_6$
	$C_5H_5Fe[P(OPh)_3]_2I$		~0.57^b	0.286		$[C_5H_5Fe\{P(OPh)_3\}_2I]PF_6$
(c)	$C_5H_5Fe(CO)(CNPh)I$		0.95	0.044		$[C_5H_5Fe(CO)(CNPh)_2]PF_6$ ^{f}
	$C_5H_5Fe(CNPh)_2I$		0.58	0.074		$[C_5H_5Fe(CNPh)_3]PF_6$
(d)	$C_5H_5Mn(CO)(diphos)$		0.007	0.064	$[C_5H_5Mn(CO)diphos]PF_6$	
	$C_5H_5Mn(CO)(PPh_3)_2$		−0.09	0.060	(dec.)	$[C_5H_5Mn(NO)(CO)PPh_3]PF_6$
	$C_5H_5Mn(CO)_2PPh_3$		0.71	0.095		
(e)	$Mn(CNPh)_5X$	Cl	0.29, 1.15	0.060, 0.065	$[Mn(CNPh)_6]PF_6$	
		Br	0.32, 1.17	0.065, 0.110		
		$SnCl_3$	0.86	0.090		
	$Mn(CNPh)_4(CO)I$		0.76	0.080	$[Mn(CNPh)_5(CO)]PF_6$	
	$Mn(CNPh)_3(CO)_2I$		1.21	0.160		

[a] Average of cathodic and anodic peak potentials in volts vs. saturated calomel electrode (aq. KCl) solutions in CH_2Cl_2 (~5 X 10^{-3} *M*) with $[N(C_4H_9)_4]ClO_4$ (0.1 *M*) as base electrolyte [b] Anodic peak poorly defined; generally a lower than expected current is observed. [c] Criterion for electrochemical reversibility $|E_{p,c}-E_{p,a}| < 0.059$ V. [d] Appropriate analysis obtained for all new compounds. [e] $[C_5H_5Fe(diphos)Cl]PF_6$ isolated in small yield. [f] H_2O_2 oxidation in acetone.

$C_5H_5FeL_2X$, MnL_5X and $RC_5H_4Mn(CO)_{3-x}L_x$ were obtained using cyclic voltammetry (Table 1). Since one of the concerns in this work was to determine the influence of various ligand groups, the ligands L and X were varied, L among phosphines, phosphites and isocyanides, X among several typical groups including halogen, methyl, hydrogen and SnX_3. Illustrative of this work are the data on the $C_5H_5Fe(diphos)X$ complexes (Series a). Generally these complexes are very easy to oxidize, the single exception observed here being the complex having X = $SnCl_3$ which differs substantially from the other complexes, presumably due to the electron-withdrawing capacity of the $SnCl_3$ group. Otherwise the order of ease of oxidation is anticipated, with the compounds for which X = CH_3 and H being easiest to oxidize, the halide complexes less so. It is interesting to note that the $E_{1/2}$ values for the halide complexes are quite similar, though their order is reversed from that predicted by electronegativity considerations. This result was also observed in the $[Cr(CO)_5X]^-$ series [5].

The influence of the ligand L can be seen upon comparison of the $E_{1/2}$ values for $C_5H_5Fe(diphos)I$, $C_5H_5Fe[P(OPh)_3]_2I$, and $C_5H_5Fe(CNPh)_2I$, which increase in the order 0.15, 0.57 (poorly defined) and 0.58 V. The isocyanide and phosphite ligands are clearly lesser donors of electron density to the metal than is the phosphine ligand. A comparison between two phosphine ligands is also seen with $C_5H_5Mn(CO)(diphos)$, $E_{1/2} = -0.05$ V, and $C_5H_5Mn(CO)(PPh_3)_2$, $E_{1/2} = -0.09$ V; the latter complex is slightly easier to oxidize, though the difference is small.

The electrochemical data indicate that the phosphine complexes should be readily oxidized; indeed, this was often found to be the case, with $AgPF_6$ in acetone being an appropriate chemical oxidant, silver metal being deposited (eqns. 1,2).

$$C_5H_5Fe(diphos)X + AgPF_6 \rightarrow [C_5H_5Fe(diphos)X]PF_6 + Ag \qquad (1)$$

(X = Cl, Br, I, CH_3, $SnMe_3$)

$$RC_5H_4Mn(CO)(diphos) + AgPF_6 \rightarrow [RC_5H_4Mn(CO)diphos]PF_6 + Ag \qquad (2)$$

The products, crystalline solids, were isolated in good yields (50%) using standard techniques. They are paramagnetic, with magnetic moments corresponding to one unpaired electron.

Considerably higher resistance to oxidation of the isocyanide and phosphite complexes was suggested by the electrochemical data. Oxidation of these species was generally not possible using $AgPF_6$; however in one instance, use of the stronger oxidizing agent $NOPF_6$ [6] leads to a 17*e* species (eqn. 3).

$$C_5H_5Fe[P(OPh)_3]_2I + NOPF_6 \rightarrow [C_5H_5Fe\{P(OPh)_3\}_2I]PF_6 + NO \qquad (3)$$

There were certain instances, however, where anticipated oxidation reactions were not observed. The attempted oxidation of $Mn(CNPh)_5X$ species, which were predicted by the $E_{1/2}$ values to be easy, and the oxidations of $Mn(CNPh)_4(CO)I$, $CpFe(CNPh)_2I$ and $CpFe(CO)(CNPh)I$, which should be somewhat more difficult, are noted. In each instance the only reaction occurring on attempted oxidation was halide ion replacement by an isocyanide ligand. The Ag^+ assisted loss of an X^- ion from these complexes is clearly facile;

it must occur at a rate greater than the rate of electron transfer. It is quite possible that halide loss is promoted by the high electron density of the metal. The resulting intermediate, probably complexed by the solvent, rapidly adds free ligand which is present from the degradation of this intermediate species in the reaction.

These observations suggest application of these methods for the syntheses of new mixed ligand complexes. We have carried out reactions of $AgPF_6$ with $Mn(CNPh)_5Cl$ and with $Mn(CNPh)_4(CO)Cl$ in liquid MeNC. These reactions occur readily with specific formations of $[Mn(CNPh)_5(CNMe)]PF_6$ and *cis*-$[Mn(CNPh)_4(CO)(CNMe)]PF_6$ (eqn. 4,5) in high yields.

$$Mn(CNPh)_5Cl + AgPF_6 \xrightarrow{CNMe} [Mn(CNPh)_5(CNMe)]PF_6 + AgCl \qquad (4)$$

$$Mn(CNPh)_4(CO)Cl + AgPF_6 \xrightarrow{CNMe} [Mn(CNPh)_4(CO)(CNMe)]PF_6 + AgCl \qquad (5)$$

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References

1 P.M. Treichel, G.E. Dirreen and H.J. Mueh, J. Organometal. Chem., 44 (1972) 339.
2 P.M. Treichel and G.E. Dirreen, J. Organometal. Chem., 39 (1972) C20.
3 A.C. Sarapu, Ph.D. Thesis, University of Wisconsin, Madison, 1972.
4 P.M. Treichel and K.P. Wagner, Inorg. Chem., submitted for publication.
5 A.M. Bond, J.A. Bowden and R. Colton, Inorg. Chem., 13 (1974) 602.
6 M.T. Mocella, M.S. Okamoto, and E.K. Barefield, Syn. React. Inorg. Metal-Org. Chem., 4 (1974) 69.