Reactions of Tricarbonyl(η-hexamethylbenzene)chromium Derivatives with Nitrosonium and Benzenediazonium Ions: Reversible Oxidation *versus* Nitrosyl- or Areneazo-complex Formation

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The complexes $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, or $P(OMe)_3$] react with $[NO][PF_6]$ to afford $[Cr(CO)L(\eta\text{-}C_6Me_6)(NO)][PF_6]$, (I), and $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ whereas $[PhN_2][PF_6]$ yields paramagnetic $[Cr(CO)_2L(\eta\text{-}C_6Me_6)][PF_6]$ (L = PPh_3, $PMePh_2$, or PMe_2Ph) or $[Cr(CO)L(\eta\text{-}C_6Me_6)(N_2Ph)][PF_6]$ and $[Cr(CO)_2(\eta\text{-}C_6Me_6)(N_2Ph)][PF_6]$ [L = $P(OMe)_3$ or $P(OPh)_3$]. Electrochemical studies confirm that oxidation of $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ to $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]^+$ is a reversible one-electron process. The factors determining whether $[NO]^+$ or $[PhN_2]^+$ oxidise organometallic complexes or cause substitution are discussed on the basis of the electrochemical and preparative results, and a general mechanism for the reactions of these ions with organotransition-metal complexes is proposed.

IN our studies of the reactions of the nitrosonium ion, $[NO]^+$, with transition-metal complexes we have found a wide variety of reaction products.[1] In favourable circumstances formation of cationic nitrosyl species may be achieved[2] whereas reversible one-electron oxidation[3] or, in methanol, protonation[1,4,5] may also occur. In acetonitrile the formation of complexes containing the solvent as ligand has also been observed.[5,6] In view of the wide use recently made of $[NO]^+$ as a reagent in organometallic syntheses[7] it seemed important to attempt to determine the factors which govern the formation of the various possible products.

It has already been noted[8] that $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)]$ and $[NO][PF_6]$ afford a mixture of $[Cr(CO)(PPh_3)(\eta\text{-}C_6Me_6)(NO)][PF_6]$ and $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$, and that diazonium salts afford $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)]^+$ by oxidation.[9] In addition, other workers[10,11] have reported that strong acids such as CF_3CO_2H protonate $[Cr(CO)_2(PPh_3)(\eta\text{-arene})]$ to give $[Cr(CO)_2H(PPh_3)(\eta\text{-arene})]^+$. Since the properties of $[Cr(CO)_2L(\eta\text{-arene})]$ may be varied substantially by changing L or the arene, and protonation, oxidation, and nitrosonium-ion substitution have all been observed in the reactions of these species, we have prepared a series of phosphine and phosphite derivatives of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ and thereby attempted to determine some of the factors influencing the behaviour of $[NO]^+$ towards organometallic substrates. By correlating the chemical behaviour of $[NO]^+$, and the closely related benzenediazonium ion, towards $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ with electrochemical studies on the latter, we have been able to make estimates of the potentials at which $[NO]^+$, and $[PhN_2]^+$, preferentially oxidise $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ rather than displace a carbonyl ligand. In addition we propose a mechanism by which either oxidation or nitrosonium- and benzenediazonium-ion substitution of a transition-metal complex can occur, and which also explains the general observation that carbonyl substitution by these ions is always far more rapid than is substitution by Lewis bases such as phosphines and isocyanides.

RESULTS AND DISCUSSION

Synthetic Studies.—Addition of solid $[NO][PF_6]$ to $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, or $P(OMe)_3$] in methanol–toluene mixtures afforded orange solutions from which orange-yellow solids were precipitated either on standing or on addition of diethyl ether. In every case the product was a mixture of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$,[2] formed by phosphine or phosphite displacement, and $[Cr(CO)L(\eta\text{-}C_6Me_6)(NO)][PF_6]$, (I). The mixture was separated either by washing with small portions of methanol, to remove the dicarbonylnitrosyl complex (L = PPh_3), or by fractional crystallisation from CH_2Cl_2–hexane mixtures [L = $P(OMe)_3$ or $P(OPh)_3$]. Where L = $PMePh_2$ or PMe_2Ph separation was not achieved. Complexes (I) are orange air-stable crystalline solids which dissolve in polar solvents to give moderately air-stable orange solutions. The complexes were characterised by microanalysis (C, H, and N) and by i.r. and ^1H n.m.r. spectroscopy (Tables 1 and 2). Although the yields of the nitrosyl phosphine cations were only moderate (30—50%) attempts to prepare them in larger amounts by direct substitution were unsuccessful. Heating $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ under reflux with L in acetone or methanol resulted mainly in decomposition although i.r. evidence for production of the $PMePh_2$ and PMe_2Ph derivatives was obtained. The relative unreactivity of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ towards substitution is somewhat surprising; the isoelectronic complex

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[4] B. F. G. Johnson and J. A. Segal, *J. Organometallic Chem.*, 1971, **31**, C79.

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[6] N. G. Connelly, M. Green, and T. A. Kuc, *J.C.S. Chem. Comm.*, 1974, 542.

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[9] N. G. Connelly and Z. Demidowicz, *J. Organometallic Chem.*, 1974, **73**, C31.

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[11] B. V. Loshkin, V. I. Zdanovich, N. K. Baranetskaya, V. N. Setkina, and D. N. Kursanov, *J. Organometallic Chem.*, 1972, **37**, 331.

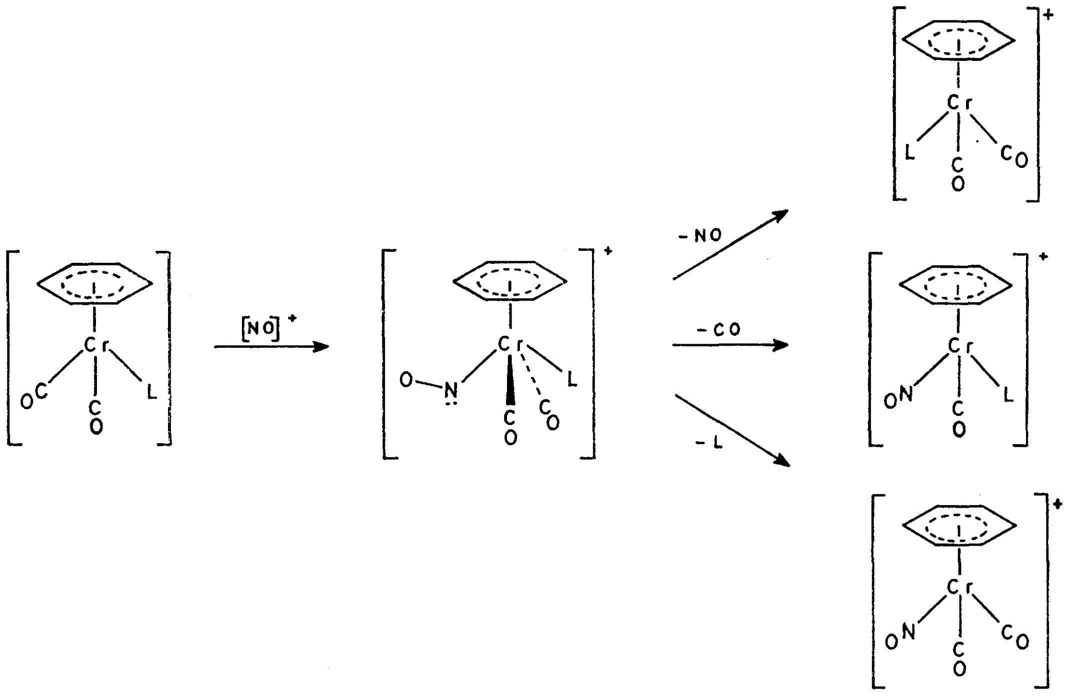
$[Mn(CO)_2(\eta\text{-}C_5H_5)(NO)][PF_6]$ undergoes phosphine substitution readily.[12-14]

TABLE 1

I.r., analytical, and m.p. data for $[Cr(CO)L(\eta\text{-}C_6Me_6)(NO)][PF_6]$, (I), and $[Cr(CO)L(\eta\text{-}C_6HMe_6)(NO)]$, (II)

Complex	L	M.p. (θ_c/°C)	Yield/%	Analyses [a]/% C	H	N	I.r. spectra (cm^{-1}) [b] ν(CO)	ν(NO)
(I)	$P(OPh)_3$	decomp. >165	33	50.7 (51.2)	4.5 (4.6)	2.2 (1.9)	1 998	1 722
(I)	$P(OMe)_3$	decomp. >145	49	35.0 (35.5)	5.0 (5.0)	2.8 (2.6)	1 983	1 713
(I)	PPh_3	176	43	54.3 (54.8)	5.0 (4.9)	1.8 (2.1)	1 983	1 703
(I)	$PMePh_2$	c	c		c		1 973	1 706
(I)	PMe_2Ph	c	c		c		1 968	1 700
(II)	$P(OPh)_3$	decomp. >165	16	63.4 (63.8)	5.9 (5.9)	2.2 (2.4)	1 944 [d]	1 651
(II)	PPh_3	decomp. >130	c	69.3 (69.5)	6.4 (6.4)	2.6 (2.6)	1 917 [d]	1 634

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] Not measured. [d] In hexane.



SCHEME

TABLE 2

^1H N.m.r. spectra (τ) of $[Cr(CO)L(\eta\text{-}C_6Me_6)(NO)][PF_6]$

L	Arene protons [a]	L protons [a]
PPh_3	7.87 (18, s)	2.37 (15, m) [b]
$P(OPh)_3$	7.65 (18, s)	2.67 (15, m) [c]
$P(OMe)_3$	7.60 (18, s)	6.12 (9, d) [b,d]

[a] The intensity and multiplicity are given in parentheses; s = singlet, d = doublet, and m = multiplet. [b] In $(CD_3)_2CO$. [c] In CD_3NO_2. [d] J_{PH} 11.2 Hz.

Complexes [I; $L = PPh_3$ or $P(OPh)_3$] reacted with $Na[BH_4]$ in tetrahydrofuran (thf) to afford orange solutions from which, on evaporation to dryness, extraction into hexane, and cooling to −80 °C, the neutral η-cyclohexadienyls $[Cr(CO)L(\textit{endo}\text{-}C_6HMe_6)(NO)]$, (II), were obtained. In the case of $L = PPh_3$ difficulty in isolating the complex in sufficient quantities precluded full ^1H n.m.r. characterisation. The orange crystalline triphenyl phosphite complex, however, was isolated in greater yield (16%). Its ^1H n.m.r. spectrum showed the six methyl groups of the cyclohexadienyl ring to be inequivalent, such inequivalence arising from the chiral nature of the chromium atom. An unambiguous assignment of the spectrum was not possible but arguments used previously[2,15] suggest the following to be reasonable: τ (in C_6D_6) 8.86 (3, d, J_{HH} 7) (Me_6), 8.47 (3, s), 8.44 (3, s) ($Me_{1,5}$), 8.31 (3, s), 8.22 (3, s) ($Me_{2,4}$), 7.98 (3, d, J_{PH} 1.5 Hz) (Me_3), and 2.82 (15, m) $[P(OC_6H_5)_3]$. The high-field signal, due to the *endo*-methyl group, was split by coupling to the *exo*-proton (J_{HH} 7 Hz) but the signal due to the latter was obscured by the remaining methyl resonances. Each methyl resonance was also split by coupling to the ^{31}P nucleus of the phosphite ligand. Only for Me_3, however, is the coupling (J_{PH} 1.5 Hz) larger than 1 Hz.

Electrochemical Studies.—Cyclic-voltammetric studies in CH_2Cl_2 showed that $[Cr(CO)_2(L)(\eta\text{-}C_6Me_6)]$ undergo

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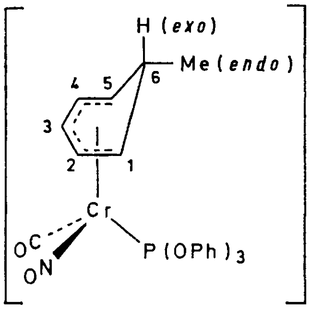
[12] T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1970, 850.

[13] H. Brunner, *Z. anorg. Chem.*, 1969, **368**, 120.

[14] R. B. King and A. Efraty, *Inorg. Chem.*, 1969, **8**, 2374.

[15] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (C), 1968, 2257.

oxidation at the stationary platinum-wire electrode. Although the complexes slowly decomposed even under carefully controlled anaerobic conditions, the electrochemical data obtained, when compared with that for $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^{2-} \rightleftharpoons [\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^{-} + e^{-}$ (see Experimental section), confirm the first oxidation step to be a reversible one-electron process corresponding to formation of $[\mathrm{Cr(CO)_2(L)(\eta\text{-}C_6Me_6)}]^{+}$. At higher potentials further, irreversible, oxidation processes occurred, probably corresponding to loss of the co-ordinated ligand L. The potentials, E_p, for the reversible oxidations (Table 3) varied between 0.23 and −0.11 V [relative to a standard calomel electrode (s.c.e.), 1M in LiCl] and are *ca.* 300—600 mV more negative than that measured[16] for $[\mathrm{Cr(CO)_3(\eta\text{-}C_6Me_6)}]$ (E_p 0.55 V). The shift of E_p to a more negative potential on substitution of a carbonyl ligand by a donor, L, is as expected.



(II) L = P(OPh)$_3$

TABLE 3

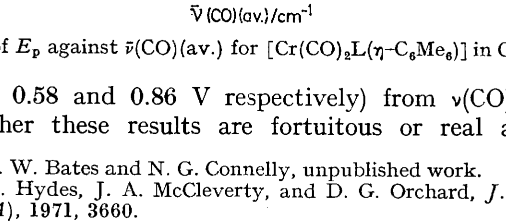
I.r. and electrochemical data [a] for $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]^z$

L	z	$\bar{\nu}$(CO) [b]/cm^{-1}	E_p/V	$(E_p)_c - (E_p)_a$/mV	$(i_p)_c$/μA	$(i_p)_a$/μA
P(OPh)$_3$	0	1 886, 1 825	0.23	160	2.7	2.8
P(OMe)$_3$	0	1 870, 1 808	0.08	177	2.8	3.2
PPh$_3$	0	1 857, 1 796	−0.05	155	1.7	1.7
	+1	1 969, 1 853				
PMePh$_2$	0	1 853, 1 793	−0.08	180	3.2	3.7
	+1	1 965, 1 849				
PMe$_2$Ph	0	1 850, 1 787	−0.11	175	2.5	2.8
	+1	1 961, 1 849				

[a] For the reversible one-electron oxidation of $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^{2-}$: $(E_p)_c - (E_p)_a = 155$ mV; $(i_p)_c = 3.0$ μA; $(i_p)_a = 3.0$ μA. [b] In CH$_2$Cl$_2$.

The general dependence of E_p on L is analogous to that of ν(CO) on L. Thus, an increase in the donor ability of L leads to a decrease both in E_p and ν(CO) such that E_p [and ν(CO)] for $\mathrm{P(OPh)_3 > P(OMe)_3 > PPh_3 > PMePh_2 > PMe_2Ph}$. A plot of E_p against either the average value of the two carbonyl-stretching frequencies, ν(CO)(av.), or the carbonyl-stretching frequency of the A_1 mode, ν(CO)(A_1), for $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$, reveals that the relation between E_p and ν(CO) is not only general but linear (Figure). Such linear correlations between ν(CO) and E_p have previously been noted for $[\mathrm{Co(CO)_2L(NO)}]$ (L = phosphines, arsines, *etc.*)[17] and for $[\mathrm{\{Fe(CO)(\eta\text{-}C_5H_4Me)(SR)\}_2}]$ (R = alkyl or aryl),[18] and also between ν(NO) and E_p[19] for $[\mathrm{MnL(L')(\eta\text{-}C_5H_5)(NO)}]^z$ (L, L′ = nitrogen-, phosphorus-, or sulphur-donor ligands; $z = -1, 0,$ or $+1$). The reasons for such direct correlations are not completely clear but a discussion of some of the factors involved has appeared[17] and will not be repeated here. It is, however, of interest to note that the existence of such linear relations implies that the straightforward measurement of ν(CO) [or ν(NO)] for an electrochemically active complex can allow prediction of the oxidation potential of that complex and hence its behaviour towards a wide range of redox reagents. In the specific case of the data reported here it should now be possible to predict the oxidation potentials of any of the phosphine, phosphite, or similar π-bonding ligand derivatives of $[\mathrm{Cr(CO)_3(\eta\text{-}arene)}]$. The data may, for example, be used to explain the apparent lack of redox activity of $[\mathrm{Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)}]^{+}$ which is isoelectronic with the phosphine and phosphite derivatives under study. Based on ν(CO)(av.) (2 040 cm^{-1}), E_p for the dicarbonylnitrosyl cation would occur at *ca.* 1.9 V, outside the range in which measurements can be made with the electrochemical system presently in use.

Whether the correlation between E_p and ν(CO) for $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ can be used to predict oxidation potentials for closely related isoelectronic species such as $[\mathrm{Mn(CO)_2L(\eta\text{-}C_5H_5)}]$ is a matter for speculation. Preliminary measurements[20] for $[\mathrm{Mn(CO)_2L(\eta\text{-}C_5H_4Me)}]$ [L = PEt$_3$, PPh$_3$, or P(OPh)$_3$] show good agreement between the determined values for E_p {0.44(PEt$_3$), 0.55 (PPh$_3$), and 0.87 V [P(OPh)$_3$]} and those calculated (0.48, 0.58 and 0.86 V respectively) from ν(CO)(av.). Whether these results are fortuitous or real awaits



Plot of E_p against $\bar{\nu}$(CO)(av.) for $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ in CH$_2$Cl$_2$

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[16] M. K. Lloyd, J. A. McCleverty, J. A. Connor, and E. M. Jones, *J.C.S. Dalton*, 1973, 1768.

[17] J. Mašek, *Inorg. Chim. Acta Rev.*, 1969, **3**, 99.

[18] J. W. Bates and N. G. Connelly, unpublished work.

[19] P. Hydes, J. A. McCleverty, and D. G. Orchard, *J. Chem. Soc.* (*A*), 1971, 3660.

[20] N. G. Connelly and M. D. Kitchen, unpublished work.

further study on a wider range of derivatives; should they be real, correlations between E_p and ν(CO) take on a greater significance.

It is important to note at this point that for certain series of complexes for which there is a linear correlation between E_p and ν(CO) there are members of those series for which deviations from the linear plot occur. For example data [3] for $[\mathrm{Cr(CO)_2(PhC{\equiv}CPh)(\eta\text{-}C_6Me_6)}]$ [ν(CO)(av.) at 1 861 cm^{-1}; E −0.22 V] and related acetylene derivatives do not correlate with those measured for the phosphorus-donor ligand complexes, and for certain substituents, R, good agreement is not found for E_p against ν(CO) for $[\{\mathrm{Fe(CO)(\eta\text{-}C_5H_4Me)(\mu\text{-}SR)}\}_2]$.[18] Mašek [17] pointed out that deviations from the linear correlations may be due to special steric and electronic factors. Thus, in the case of the η-acetylene derivatives cited above the apparently anomalous data may arise from the considerable difference in bonding between metals and η-acetylenes and between metals and phosphines or phosphites. For the dimeric iron species deviation from the linear relation between ν(CO) and E_p, observed for substituents such as benzyl and t-butyl, may well be caused by steric factors. Experiments designed to determine the effects of steric requirements on E_p are in progress in this laboratory.

As well as the correlation between E_p and ν(CO), the electrochemical data gathered for $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ allow certain conclusions to be drawn with respect to the ability of $[\mathrm{NO}]^+$ and $[\mathrm{PhN_2}]^+$ to act as one-electron oxidants or precursors to nitrosyl- or areneazo-metal complexes. In $\mathrm{CH_2Cl_2}$, as well as in methanol–toluene, $[\mathrm{NO}]^+$ reacts with $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ (L = phosphines or phosphites) to afford only substituted nitrosyl-containing products, no evidence for the formation of oxidised species being observed. It has, however, been shown previously [3] that for $\mathrm{L = PhC{\equiv}CPh}$ reversible one-electron oxidation by $[\mathrm{NO}]^+$ occurs to afford $[\mathrm{Cr(CO)_2(PhC{\equiv}CPh)(\eta\text{-}C_6Me_6)}]^+$. On consideration of the oxidation potentials for the neutral complexes it is therefore possible to estimate the potential, $E(\mathrm{NO}^+)$, at which $[\mathrm{NO}]^+$ will preferentially oxidise $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ as being between E_p for $\mathrm{L = PhC{\equiv}CPh}$ and $\mathrm{PPhMe_2}$, *i.e.* $-0.22 < E(\mathrm{NO}^+) < -0.11$ V.

We have noted elsewhere [9] that $[\mathrm{PhN_2}]^+$ oxidises $[\mathrm{Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)}]$ to the corresponding paramagnetic monocation ($\langle g_\mathrm{av.}\rangle$ 2.041; $\langle A_\mathrm{p(av.)}\rangle$ 31.3 G).* Monitoring the reactions of $[\mathrm{PhN_2}]^+$ with the remaining phosphine and phosphite derivatives in $\mathrm{CH_2Cl_2}$ allows an estimate to be made of the potential $E(\mathrm{PhN_2}^+)$ at which $[\mathrm{PhN_2}]^+$ will preferentially oxidise $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$. Thus, for $\mathrm{L = PMePh_2}$ and $\mathrm{PMe_2Ph}$, rapid generation of $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]^+$ occurs [ν(CO) at 1 965 and 1 849 cm^{-1} ($\mathrm{PMePh_2}$) and 1 961 and 1 849 cm^{-1} ($\mathrm{PMe_2Ph}$)]. Their e.s.r. spectra at −196 °C are similar to that of the $\mathrm{PPh_3}$ complex, showing three-fold anisotropy of the $\langle g \rangle$ factor and ^{31}P hyperfine coupling. By contrast, for $\mathrm{L = P(OMe)_3}$ and $\mathrm{P(OPh)_3}$ only mixtures of $[\mathrm{Cr(CO)L(\eta\text{-}C_6Me_6)(N_2Ph)}]^+$ and $[\mathrm{Cr(CO)_2(\eta\text{-}C_6Me_6)(N_2Ph)}]^+$ result. The reactions between $[\mathrm{PhN_2}]^+$ and $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ therefore allow $E(\mathrm{PhN_2}^+)$ to be estimated, *i.e.* $-0.05 < E(\mathrm{PhN_2}^+) < +0.08$ V. It should be noted that, unlike the nitrosonium ion, substituents on the aryl group of the diazonium cation cause a change in $E(\mathrm{RN_2}^+)$.[21]

With $E(\mathrm{NO}^+)$ and $E(\mathrm{PhN_2}^+)$ now estimated it is possible to discuss the factors which cause the nitrosonium and benzenediazonium ions to either oxidise or undergo substitution reactions with transition-metal complexes. It might be expected that $E(\mathrm{NO}^+)$ and $E(\mathrm{PhN_2}^+)$ represent the true oxidation potentials for the couples NO–$[\mathrm{NO}]^+$ and $\mathrm{PhN_2}$–$[\mathrm{PhN_2}]^+$ in that complexes $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$ with E_p greater than $E(\mathrm{NO}^+)$ or $E(\mathrm{PhN_2}^+)$ undergo substitution whereas those with lower E_p undergo oxidation. It is, however, obvious that $E(\mathrm{NO}^+)$ and $E(\mathrm{PhN_2}^+)$ are far too low to be the true values for the oxidation potentials of NO–$[\mathrm{NO}]^+$ and $\mathrm{PhN_2}$–$[\mathrm{PhN_2}]^+$. Not only is it unrealistic to assume that $[\mathrm{NO}]^+$ is a weaker oxidising agent than $[\mathrm{PhN_2}]^+$, as suggested by the relative values of $E(\mathrm{NO}^+)$ and $E(\mathrm{PhN_2}^+)$ but it has also been found that for several species oxidation by $[\mathrm{NO}]^+$ or $[\mathrm{PhN_2}]^+$ occurs even though E_p for that species is far greater than $E(\mathrm{NO}^+)$ or $E(\mathrm{PhN_2}^+)$ estimated from the data found for the arenechromium complexes. Thus ferrocene, $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}]$ (E_p 0.38 V), is oxidised to the ferricinium ion by $[\mathrm{NO}]^+$ and by $[\mathrm{PhN_2}]^+$, and $[\mathrm{Cr(CO)_4(dppe)}]$ (E_p 0.64 V) is oxidised by $[\mathrm{NO}]^+$ to $[\mathrm{Cr(CO)_4(dppe)}]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane]. In addition, although the oxidation potentials for the couples NO–$[\mathrm{NO}]^+$ and $\mathrm{PhN_2}$–$[\mathrm{PhN_2}]^+$ have not been directly measured under conditions identical to those used in our electrochemical studies, they have been found to be 1.58 V (relative to an Ag–AgCl electrode, in nitromethane [22]) and 0.295 V (relative to a s.c.e. in sulfolane [21]) respectively. It is therefore apparent that the behaviour of $[\mathrm{NO}]^+$ and $[\mathrm{PhN_2}]^+$ towards transition-metal complexes is not governed solely by the oxidation potential of the complex and that substitution reactions can occur even with complexes with relatively low E_p values.

In order to explain this observation we propose a general mechanism for $[\mathrm{NO}]^+$ and $[\mathrm{PhN_2}]^+$ reactions, illustrated in the Scheme for the reaction of $[\mathrm{NO}]^+$ with $[\mathrm{Cr(CO)_2L(\eta\text{-}C_6Me_6)}]$. The first step in the sequence is addition of $[\mathrm{NO}]^+$ to the metal atom to form an intermediate in which the nitrosyl ligand is bonded in a ' bent ' fashion and is therefore co-ordinated formally as $[\mathrm{NO}]^-$. Such an addition is not without precedent; $[\mathrm{IrCl(CO)(PPh_3)_2(NO)}]^+$, in which the Ir–N–O angle [23] is 124°, results from reaction between $[\mathrm{NO}]^+$ and $[\mathrm{IrCl(CO)(PPh_3)_2}]$. Addition of $[\mathrm{PhN_2}]^+$ to afford the analogous ' $[\mathrm{PhN_2}]^-$ ' complex is also possible, since the formation of ' bent ' and ' linear ' areneazo-complexes is also well authenticated. The intermediate may then lose nitrogen mono-

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* 1 G = 10^{-4} T.

[21] R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 1969, **34**, 854.

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oxide to form $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]^+$ or a carbonyl or ligand L to form a substituted nitrosyl cation $[Cr(CO)L(\eta\text{-}C_6Me_6)(NO)]^+$ or $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$. In the latter cases, loss of the ligand and straightening of the Cr–N–O angle will result in the nitrosyl ligand bonding normally as $[NO]^+$ and thus functioning as a three-electron donor. Such a mechanism not only accounts for the products observed in the reaction of $[NO]^+$ with $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ but also for the observation that substitution reactions of the nitrosonium ion with transition-metal carbonyl derivatives invariably occur much more rapidly, and under much milder conditions, than those with other neutral donor ligands. As an illustration, $[NO]^+$ reacts with $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ in seconds, at room temperature, to afford $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$, whereas substitution by phosphine ligands is achieved by u.v. irradiation for prolonged periods. The S_N2-type reaction proposed, in which the initial rapid addition of $[NO]^+$ to form a cation will cause immediate chromium–carbonyl and –phosphorus bond weakening because of reduced back donation from the positively charged metal, will be much more rapid than the S_N1-type substitution by phosphines which requires chromium–carbonyl bond cleavage in the neutral complex $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$. In support of the suggested mechanism it has already been shown that whereas $[Co(CO)_3(NO)]$ undergoes S_N2 substitution,[24] *via* the intermediate $[Co(CO)_3(NO)L]$ in which the nitrosyl ligand becomes 'bent' and formally a one-electron donor, the isoelectronic carbonyl $Ni(CO)_4$ undergoes a dissociative, S_N1, reaction *via* the intermediate $Ni(CO)_3$.

Consideration of the bonding in the intermediate $[Cr(CO)_2L(\eta\text{-}C_6Me_6)(NO)]^+$ also allows an interpretation of the significance of $E(NO^+)$ and $E(PhN_2^+)$. The $[NO]^-$ ligand is formally a one-electron donor, behaving in a similar manner to halide, and participating little in back bonding from metal to nitrogen. Thus as the donor ability of L decreases the Cr–N bond strength is likely to increase with the increased positive charge on the metal. The decrease in donor ability of L, however, will also bring about a decrease in the amount of back bonding from the metal to the carbonyl groups thus causing a decrease in the Cr–C bond strengths. The potential $E(NO^+)$ or $E(PhN_2^+)$ is thus a measure of the point at which Cr–C rather than Cr–N bond cleavage occurs to give the substituted rather than the oxidised product. The relative values of $E(NO^+)$ and $E(PhN_2^+)$ can now also be explained. That $E(PhN_2^+)$ is more positive than $E(NO^+)$ does not mean that the benzenediazonium ion is a better oxidising agent than nitrosonium ion, rather that the Cr–N bond strength in the intermediate $[Cr(CO)_2L(\eta\text{-}C_6Me_6)(N_2Ph)]^+$ is lower than that of the Cr–N bond in the nitrosyl analogue. Such an explanation is in keeping with the observation[25] that $[NO]^+$ replaces $[PhN_2]^+$ from $[IrCl(PPh_3)_2(N_2Ph)]^+$ to form the corresponding nitrosyl complex $[IrCl(PPh_3)_2(NO)]^+$. Finally, since the potential $E(NO^+)$ or $E(PhN_2^+)$ at which nitrosyl or areneazo-complex formation occurs rather than oxidation depends on relative bond strengths in the intermediate, such potentials are likely to vary from metal to metal and hence differ for one set of complexes to another. We must conclude, therefore, that $E(NO^+)$ and $E(PhN_2^+)$ measured for $[Cr(CO)_2L(\eta\text{-arene})]$ may not be applicable to other series of organometallic complexes. For organometallics, such as ferrocene, where substitution to form cationic nitrosyl or areneazo-complexes is highly unlikely, oxidation will occur unless the oxidation potential of the complex is greater than the *real* value for the couple NO–$[NO]^+$ or PhN_2–$[PhN_2]^+$.

Conclusion.—Studies on the reactions of $[NO]^+$ and $[PhN_2]^+$ with $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ have shown that formation of oxidised or substituted products depends on the relative metal–ligand bond strengths in the proposed intermediate $[Cr(CO)_2L(\eta\text{-}C_6Me_6)(X)]^+$ ($X =$ NO or PhN_2) rather than the reduction potential of the nitrosonium or benzenediazonium cations.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of nitrogen. $[Cr(CO)_2L(\eta\text{-}C_6Me_6)]$ were prepared by u.v. irradiation of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ and a phosphine, L, in toluene or hexane, or by displacement of PhC≡CPh from $[Cr(CO)_2(\eta\text{-PhC≡CPh})(\eta\text{-}C_6Me_6)]$ by L in refluxing hexane. The salt $[NO][PF_6]$ was purchased from Ozark Mahoning Co., Tulsa, Oklahoma and $[PhN_2][PF_6]$ from Aldrich Chemical Company Inc., Milwaukee, Wisconsin. All solvents were dried by standard methods and deoxygenated before use.

I.r. spectra were recorded on Perkin-Elmer PE257 or PE457 spectrophotometers using, in the case of solution spectra, the ×10 expansion facility on the former and were calibrated against the 1 601 cm^{-1} absorption of polystyrene. ^{1}H N.m.r. spectra were recorded on Varian Associates HA100 or T60 instruments and calibrated using $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Electrochemical studies were made using a Beckman Electroscan 30. Cyclic voltammetry was carried out using platinum-wire auxiliary and working electrodes and a saturated calomel electrode (1M in LiCl) as reference. Solutions were 10^{-3}M in complex and 0.05M in $[Et_4N][ClO_4]$ as supporting electrolyte. Criteria for reversibility are based on the assumption that data for the complex under study should be similar to that found for the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Dicarbonyl(η-hexamethylbenzene)triphenylphosphinechromium Hexafluorophosphate, $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)][PF_6]$.—To $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)]$ (0.50 g) in CH_2Cl_2 (25 cm^3) was added $[PhN_2][PF_6]$ (0.26 g). On stirring the yellow solution became dark brown and gas was evolved. After 25 min the solution was filtered and hexane (50 cm^3) added. The resulting yellow-brown precipitate was filtered off and recrystallised from CH_2Cl_2–hexane to afford the complex as a yellow-brown *solid*, yield 0.15 g (24%), m.p. 165—170 °C

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(decomp.) (Found: C, 55.7; H, 4.8. Calc.: C, 56.7, H, 4.9%). The complex is fairly rapidly decomposed by air and dissolves in polar solvents such as CH_2Cl_2 and acetone to give yellow air-sensitive solutions.

Carbonyl(η-hexamethylbenzene)nitrosyltriphenylphosphinechromium Hexafluorophosphate, $[Cr(CO)(PPh_3)(\eta\text{-}C_6Me_6)(NO)][PF_6]$ (I; L = PPh_3).—To a vigorously stirred solution of $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)]$ (1.10 g) in toluene–methanol (56 cm^3; 25 : 3) was added solid $[NO][PF_6]$ (0.54 g). After 5 min diethyl ether (100 cm^3) was added to complete precipitation of a mixture of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ and $[Cr(CO)(PPh_3)(\eta\text{-}C_6Me_6)(NO)][PF_6]$. Careful washing with methanol (0.5 cm^3 quantities) removed $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ leaving $[Cr(CO)(PPh_3)(\eta\text{-}C_6Me_6)(NO)][PF_6]$ as an orange *solid*, yield 0.6 g {43% based on $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$}. The complex was recrystallised from acetone–diethyl ether, and is soluble in polar solvents such as CH_2Cl_2, acetone, and nitromethane to give orange solutions which slowly decompose in air. Complexes [I; L = $P(OMe)_3$ or $P(OPh)_3$] were similarly prepared.

Carbonyl(1—5-η-endo-*hexamethylcyclohexadienyl*)*nitrosyl*(*triphenyl phosphite*)*chromium*, $[Cr(CO)\{P(OPh)_3\}(\eta\text{-}C_6HMe_6)(NO)]$ [II; L = $P(OPh)_3$].—To [I; L = $P(OPh)_3$] (280 mg) in thf (30 cm^3) was added $Na[BH_4]$ (80 mg). After vigorously stirring for 60 min the resulting orange solution was filtered and evaporated to dryness. The orange residue was then dissolved in hexane (5 cm^3). After filtration the solution was cooled to −80 °C to yield the complex as orange *crystals*, yield 35 mg (16%). The complex is soluble in most common organic solvents to give orange solutions which slowly decompose in air.

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