Notes

Further Comments on One-electron Oxidation *versus* Nitrosyl Complex Formation during the Reactions of the Nitrosyl Cation with Metal Carbonyl Derivatives†

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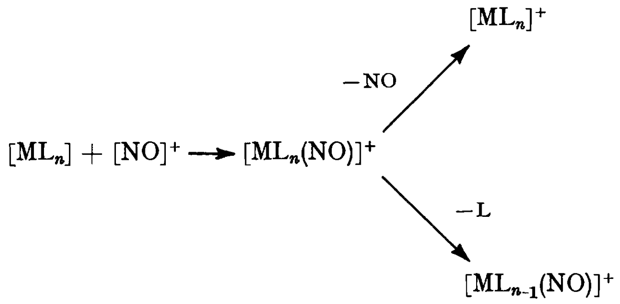
The cation $[\mathrm{NO}]^+$ reacts with $[\mathrm{M(CO)_4(L\text{–}L)}]$ [1 : M = Cr, Mo, or W; L–L = $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe) or $\mathrm{Ph_2PCH_2PPh_2}$ (dppm)] to give $[\mathrm{M(CO)_3(NO)(L\text{–}L)}]^+$(2) or, when NO is removed from the reaction mixture, $[\mathrm{M(CO)_4(L\text{–}L)}]^+$ (3; M = Cr). A modification is therefore made to the mechanism previously proposed for the reactions of $[\mathrm{NO}]^+$ with metal carbonyl derivatives, $[\mathrm{ML}_n]$, such that the intermediate adduct $[\mathrm{ML}_n\mathrm{(NO)}]^+$ is in equilibrium with $[\mathrm{ML}_n]^+$ and NO radicals. The isolation of the acid–base adducts $[\mathrm{Ag\{M(CO)_4(L\text{–}L)\}_2}]^+$ (4; M = Mo or W, L–L = dppe or dppm), from the reaction of (1) with Ag^+ ions, is indirect evidence for the formation of seven-co-ordinate intermediates, $[\mathrm{M(CO)_4(NO)(L\text{–}L)}]^+$, in the reactions between (1) and $[\mathrm{NO}]^+$.

In 1975 we proposed [2] a general mechanism (Scheme 1) for the reaction of $[\mathrm{NO}]^+$ (and $[\mathrm{N_2R}]^+$, R = aryl group) with metal carbonyl derivatives, $[\mathrm{ML}_n]$, based on the observation of *either* one-electron oxidation *or* substitution reactions for $[\mathrm{Cr(CO)_2L(\eta\text{-arene})}]$ (L = *P*-donor [2] or acetylene [3]). More recently, we have observed [4] that the product of the reaction between $[\mathrm{Mo(CO)_6}]$ and $[\mathrm{NO}]^+$ in acetonitrile depends on the experimental conditions. When evolved NO is removed from the mixture the radical $[\mathrm{Mo(NO)(NCMe)_5}]^{2+}$ is isolable but in the presence of the gas $[\mathrm{Mo(NO)_2(NCMe)_4}]^{2+}$ results. We have, therefore, further studied [5] the reactions of $[\mathrm{M(CO)_4(L\text{–}L)}]$ [1: M = Cr, Mo, or W; L–L = $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe) or $\mathrm{Ph_2PCH_2PPh_2}$ (dppm)] with $[\mathrm{NO}]^+$ salts under conditions which allow the variation of NO concentration and on the basis of the isolation of *both* $[\mathrm{M(CO)_3(NO)(L\text{–}L)}]^+$ (2) and $[\mathrm{M(CO)_4(L\text{–}L)}]^+$ (3) wish to modify the mechanism shown in Scheme 1. In addition we describe the preparation of $[\mathrm{Ag\{M(CO)_4(L\text{–}L)\}_2}]^+$ (4; M = Mo or W, L–L = dppe or dppm) from (1) and silver(I) salts and draw an analogy between these acid–base adducts and $[\mathrm{M(CO)_4(NO)(L\text{–}L)}]^+$, the intermediate postulated in the reaction between (1) and $[\mathrm{NO}]^+$.



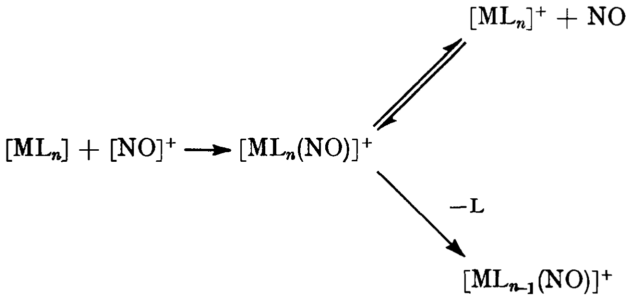
Scheme 1 $[\mathrm{ML}_n]$ = metal carbonyl derivative

RESULTS AND DISCUSSION

The reactions of (1) with $[\mathrm{NO}][\mathrm{BF_4}]$ in $\mathrm{CH_2Cl_2}$ have been carried out (*a*) in a closed nitrogen-filled vessel, and (*b*) with a vigorous stream of $\mathrm{N_2}$ gas passed through the mixture to remove the NO gas evolved. For (1; M = Mo or W) only $[\mathrm{M(CO)_3(NO)(L\text{–}L)}][\mathrm{BF_4}]$ (2; M = Mo or W) [5] is formed using either condition (*a*) or (*b*) despite the relative redox potentials of the couples NO–NO^+ and (1)—(3). The nitrosonium ion in $\mathrm{CH_2Cl_2}$ will oxidise $\mathrm{N(C_6H_4Br\text{-}}p)_3$ (E_p = 1.25 V, *vs.* a calomel electrode, 1 mol $\mathrm{dm^{-3}}$ in LiCl) to the ammonio-cation $[\mathrm{N(C_6H_4Br\text{-}}p)_3]^+$ and is, therefore, capable of oxidising (1) for which cyclic voltammetric data are given in Table 1.

By contrast, the chromium complexes (1; M = Cr) afford both (2; M = Cr) and (3; M = Cr). Under reaction condition (*a*) $[\mathrm{Cr(CO)_4(dppm)}]$ and $[\mathrm{NO}][\mathrm{BF_4}]$ give good yields of the previously unreported nitrosyl $[\mathrm{Cr(CO)_3(NO)(dppm)}][\mathrm{BF_4}]$ (Table 2), but under condition (*b*) a mixture of $[\mathrm{Cr(CO)_3(NO)(dppm)}][\mathrm{BF_4}]$ and $[\mathrm{Cr(CO)_4(dppm)}][\mathrm{BF_4}]$ is formed, with the latter predominant. For $[\mathrm{Cr(CO)_4(dppe)}]$ pure samples of $[\mathrm{Cr(CO)_4(dppe)}][\mathrm{BF_4}]$ are given by method (*b*), and (*a*) yields a mixture of $[\mathrm{Cr(CO)_3(NO)(dppe)}][\mathrm{BF_4}]$ and $[\mathrm{Cr(CO)_4(dppe)}][\mathrm{BF_4}]$. Although neither reaction condition leads to the generation of $[\mathrm{Cr(CO)_3(NO)(dppe)}][\mathrm{BF_4}]$ alone, this complex may be prepared quantitatively by adding an excess of NO gas in $\mathrm{CH_2Cl_2}$ to preformed $[\mathrm{Cr(CO)_4(dppe)}][\mathrm{BF_4}]$.

In the light of these observations we wish to make a minor but significant modification to the mechanism shown in Scheme 1, namely that the adduct $[\mathrm{ML}_n\mathrm{(NO)}]^+$ is not irreversibly dissociated into $[\mathrm{ML}_n]^+$ and NO but is in equilibrium with the radicals (Scheme 2). This



Scheme 2 $[\mathrm{ML}_n]$ = metal carbonyl derivative

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† Regarded as Part 14 in the series Reduction–Oxidation Properties of Organotransition-metal Complexes.[1]

TABLE 1

Cyclic voltammetric data for the one-electron oxidation of $[M(CO)_4(L{-}L)]$ (1)

M	L–L	$E_p{}^a$/V	$[(E_p)_{ox} - (E_p)_{red}]$/mV	$[(E_p)_{ox} - (E_p/2)_{ox}]$/mV	$[(E_p)_{red} - (E_p/2)_{red}]$/mV	$(i_p)_{ox}/(i_p)_{red}$	$(i_p)_{ox}$/μA
Cr	dppm	0.67	60	60	−61	0.92	1.7
Cr	dppe	0.75	60	58	−63	0.93	1.8
Mo	dppm	0.88 [b]		43			2.0
Mo	dppe	0.94	68	60	−58	0.95	1.8
W	dppe	0.95	60	59	−60	0.98	1.7

[a] Relative to a calomel electrode, 1 mol dm^{-3} in LiCl. [b] $(E_p)_{ox}$ only. The oxidation wave is irreversible; no reduction peak is observed at 200 mV s^{-1}.

TABLE 2

Analytical and i.r. data for cationic Group 6 metal carbonyl complexes

	Analysis [a] (%)			I.r. data [b] (cm^{-1})
Complex	C	H	N	$\tilde{\nu}$(CO)
mer-$[Cr(CO)_3(NO)(dppm)][BF_4]$	52.0 (52.7)	3.6 (3.7)	1.9 (2.2)	2 089m, 2 025vs, 1 749s [c]
$[Cr(CO)_4(dppm)][BF_4]$		*d*		2 084s, 2 033m, 1 969s
$[Ag\{Mo(CO)_4(dppm)\}_2][PF_6]$	48.6 (48.5)	3.1 (3.1)		2 037w (sh), 2 029w, 2 017w, 1 957vs, 1 919ms, 1 903ms (sh)
$[Ag\{Mo(CO)_4(dppe)\}_2][BF_4]$ [e]	49.9 (50.1)	3.2 (3.4)		2 039w, 2 023w (sh), 1 955vs, 1 921ms, 1 895ms
$[Ag\{W(CO)_4(dppe)\}_2][PF_6]$	43.7 (43.9)	3.3 (3.0)		2 033w (sh), 2 025w, 2 017w, 1 949vs, 1 909ms, 1 885ms (sh)

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2; m = medium, s = strong, w = weak, sh = shoulder. [c] $\tilde{\nu}$(NO). [d] Not isolated pure. [e] Analysed as $0.5CH_2Cl_2$ solvate.

modification allows us to make further comments concerning the competition between one-electron oxidation and substitution in the reaction between metal carbonyl derivatives and $[NO]^+$. It is clear that for a given complex, $[ML_n]$, the manipulation of reaction conditions, primarily those concerning the availability of NO gas, will cause a shift in the equilibrium as demonstrated in the selective synthesis of $[Cr(CO)_4(L{-}L)]^+$ and $[Cr(CO)_3(NO)(L{-}L)]^+$ from (1; M = Cr). However, changing the properties of L and M, in $[ML_n]$, will also markedly affect this equilibrium. Assuming that the irreversible loss of L from $[ML_n(NO)]^+$ is relatively slow, stabilisation of the adduct to dissociation into radicals will favour substitution. While ligand effects are difficult to quantify we may make some assessment of the dependence of the equilibrium on metal size.

For the reaction of $[Fe(CO)_3(PPh_3)_2]$ with $[NO][PF_6]$ steric factors will be relatively unimportant in the six-co-ordinate intermediate $[Fe(CO)_3(NO)(PPh_3)_2]^+$. Thus, despite the low oxidation potential of $[Fe(CO)_3(PPh_3)_2]$ (0.38 V), and the stability of $[Fe(CO)_3(PPh_3)_2]^+$ as an isolable crystalline salt,[6] substitution to give $[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$ is preferred.[7] By contrast, steric factors are likely to be important in the reactions between $[NO]^+$ and $[Mn(CO)_{3-n}L_n(\eta\text{-}C_5R_5)]$,[8] $[Cr(CO)_2L(\eta\text{-}C_5R_5)]$,[2] and (1) for which seven-co-ordinate intermediates are proposed. For (1), then, the smaller chromium atom leads to more ready dissociation, to $[Cr(CO)_4(L{-}L)]^+$ and NO, than do the molybdenum and tungsten atoms.

Seven-co-ordination is, of course, more likely for Mo and W than for Cr and further evidence for the increased stability of $[M(CO)_4(NO)(L{-}L)]^+$ (M = Mo or W) arises from the isolation of the stable, white or cream, crystalline acid–base adducts $[Ag\{M(CO)_4(L{-}L)\}_2]X$ (4; M = Mo or W, X = BF_4 or PF_6) (Table 2) from the reaction between (1) and AgX. Silver(I) salts in CH_2Cl_2 are strong one-electron oxidants, forming $[N(C_6H_4Br\text{-}p)_3]^+$ from the neutral amine, and indeed react with (1; M = Cr) to give $[Cr(CO)_4(L{-}L)]^+$ but not (4; M = Cr). With no i.r. spectroscopic evidence for the bonding of Ag^I to carbonyl oxygen atoms, complexes (4; M = Mo or W) are seven-co-ordinate metal–metal bonded analogues of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][BF_4]$.[9]

Although we have restricted our discussion to the reactions of $[NO]^+$ we may also comment on the apparent [2] ability of $[N_2R]^+$ (R = aryl) ions to function as stronger one-electron oxidants than $[NO]^+$ despite the far more negative reduction potential for the couple N_2R–$[N_2R]^+$. First, the steric requirements of the N_2R ligand are greater than those of NO so that $[ML_n(N_2R)]^+$ will be destabilised with respect to the formation of $[ML_n]^+$ and N_2R radicals. Secondly, the equilibrium between adduct and radicals is affected by the instability of $\cdot N_2R$; the formation of paramagnetic $[ML_n]^+$ is facilitated by the irreversible formation of N_2 and biaryl.

Conclusion.—The modified mechanism shown in Scheme 2 not only better accounts for the nature of the products formed in the reactions between $[NO]^+$, or $[N_2R]^+$, and carbonyl derivatives $[ML_n]$ but also shows that preferential oxidation or substitution may be effected by the manipulation of reaction conditions. In addition, the isolation of stable silver(I) complexes, $[Ag\{M(CO)_4(L{-}L)\}_2]^+$ provides indirect evidence for the intermediate adducts $[ML_n(NO)]^+$.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, the solid complexes are moderately stable in air and dissolve in polar solvents such as CH_2Cl_2 or acetone to give solutions which slowly decompose in air. The complexes $[M(CO)_4(L{-}L)]$ (M = Cr, Mo, or W; L–L =

dppm or dppe) were prepared by published methods.[10] Silver(I) and $[NO]^+$ salts were purchased from Fluorochem Ltd., Glossop, Derbyshire. Gaseous NO was purchased from the British Oxygen Company and purified by passage through a −78 °C trap. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer and calibrated against the absorption of polystyrene at 1 601 cm^{-1}. Electrochemical studies were made as described previously,[4] in CH_2Cl_2, 0.1 mol dm^{-3} in $[NBu^n_4][BF_4]$ as supporting electrolyte. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*tetracarbonylchromium Tetrafluoroborate*, $[Cr(CO)_4(dppe)][BF_4]$.—The salt $[NO][BF_4]$ (0.06 g, 0.51 mmol) was added to a stirred solution of $[Cr(CO)_4(dppe)]$ (0.20 g, 0.36 mmol) in CH_2Cl_2 (40 cm^3) through which a vigorous stream of nitrogen was passed. After 45 min, the purple solution was filtered, hexane (40 cm^3) was added, and partial evaporation of the solvent gave the product as a purple solid, yield 0.13 g (56%). The complex dissolves in CH_2Cl_2 or acetone to give purple solutions which very rapidly become yellow due to the reduction of the cation to $[Cr(CO)_4(dppe)]$.

[*Bis*(*diphenylphosphino*)*methane*]*tricarbonylnitrosylchromium Tetrafluoroborate*, $[Cr(CO)_3(NO)(dppm)][BF_4]$.—The complex $[Cr(CO)_4(dppm)]$ (0.40 g, 0.73 mmol) and $[NO][BF_4]$ (0.12 g, 1.03 mmol) were stirred together in CH_2Cl_2 (25 cm^3) under a blanket of nitrogen in a stoppered flask. After 1 h, the yellow solution was filtered, hexane (40 cm^3) was added, and the mixture reduced in volume to yield the yellow solid product, yield 0.38 g (83%).

Bis{[*bis*(*diphenylphosphino*)*methane*]*tetracarbonylmolybdenum*}*silver Hexafluorophosphate*, $[Ag\{Mo(CO)_4(dppm)\}_2][PF_6]$.—To a stirred solution of $[Mo(CO)_4(dppm)]$ (0.15 g, 0.25 mmol) in CH_2Cl_2 (25 cm^3) was added $Ag[PF_6]$ (0.06 g, 0.24 mmol). After 30 min, the solution was filtered through Celite to remove small quantities of silver metal, and hexane (70 cm^3) was added to yield a white precipitate. Recrystallisation from CH_2Cl_2–hexane gave the *product* as white crystals, yield 0.08 g (44%).

The complexes $[Ag\{Mo(CO)_4(dppe)\}_2][BF_4]$ (white, 48%) and $[Ag\{W(CO)_4(dppe)\}_2][PF_6]$ (cream, 50%) were prepared similarly.

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