

Nitrosyl-bridged Cyclopentadienyl-cobalt and -rhodium Cations

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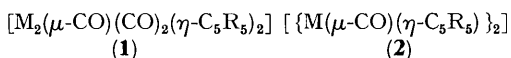
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Summary $[M(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($M = \text{Co}$ or Rh , $R = \text{H}$ or Me) and $[\text{NO}]^+$ afford $[M(\text{CO})(\text{NO})(\eta\text{-C}_5\text{R}_5)]^+$ (**3**) and then $[M_2(\text{CO})_2(\mu\text{-NO})(\eta\text{-C}_5\text{R}_5)_2]^+$ (**4**) which decarbonylates to give $[M_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-C}_5\text{R}_5)_2]^+$ (**5**); complex (**4**) undergoes reversible nitrosyl-bridge cleavage with alkenes, and (**5**) reacts with $[\text{NO}]^+$ to give $[\{M(\mu\text{-NO})(\eta\text{-C}_5\text{R}_5)\}_2]^{2+}$

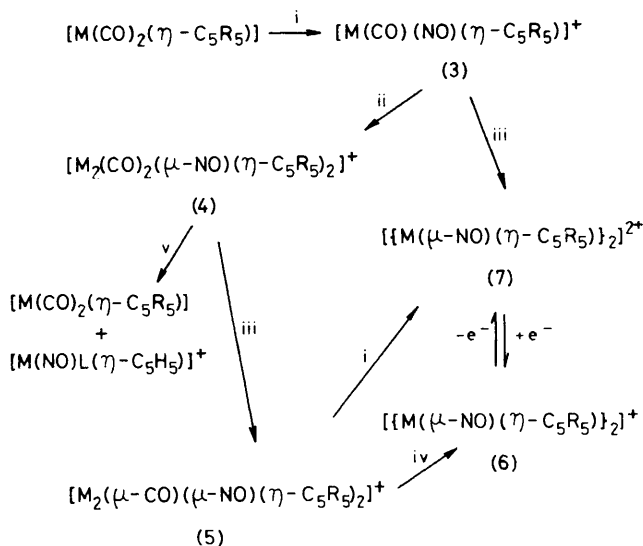
(**7**) which is reduced to $[\{M(\mu\text{-NO})(\eta\text{-C}_5\text{R}_5)\}_2]^+$ (**6**; $M = \text{Co}$).

THE binuclear cyclopentadienylmetal carbonyls $[M_2(\mu\text{-CO})(\text{CO})_2(\eta\text{-C}_5\text{R}_5)_2]$ (**1**) and $[\{M(\mu\text{-CO})(\eta\text{-C}_5\text{R}_5)\}_2]$ (**2**) ($M = \text{Co}$ or Rh , $R = \text{H}$ or Me) are of topical interest as precursors

to the ligand-bridged species $[M_2(\mu-X)(CO)_2(\eta-C_5R_5)_2]$ [$X = CR^1R^2$ (ref. 1) or SO_2 (ref. 2)] and to metal cluster complexes such as $[Co_4(\mu_2-CO)(\mu_3-CO)_2(CO)_4(\eta-C_5Me_5)_2]^3$ and $[Rh_2Pt(\mu_2-CO)_2(CO)_2(\eta-C_5Me_5)_2]^4$. We now describe the synthesis of isoelectronic, cationic nitrosyl analogues of (1) and (2) and reactions which demonstrate their potential in organometallic synthesis.



The reactions of $[NO][PF_6]$ with $[M(CO)_2(\eta-C_5R_5)]$ ($M = Co$ or Rh , $R = H$ or Me), and the subsequent pathways by which binuclear complexes are formed are shown in the Scheme. The dropwise addition of $[Co(CO)_2(\eta-C_5R_5)]$ ($R = H$ or Me) in CH_2Cl_2 to a well stirred suspension of $[NO][PF_6]$ in the same solvent results in a red-brown solution of the very reactive mononuclear complexes $[M(CO)(NO)(\eta-C_5R_5)]$ $[PF_6]$ (3; $M = Co$, $R = H$), $\tilde{\nu}(CO)$ 2130, $\tilde{\nu}(NO)$ 1900 cm^{-1} ; and (3; $M = Co$, $R = Me$), $\tilde{\nu}(CO)$ 2090, $\tilde{\nu}(NO)$ 1861 cm^{-1} ; the brown permethyl complex is isolable, in 80% yield, by precipitation with hexane. An excess of $[Co(CO)_2(\eta-C_5R_5)]$ reacts with (3) to give the brown complex $[M_2(CO)_2(\mu-NO)(\eta-C_5R_5)_2][PF_6]$ (4; $M = Co$, $R = H$), $\tilde{\nu}(CO)$ 2070 (br.), $\tilde{\nu}(NO)$ 1602 cm^{-1} , contaminated with $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5H_5)_2][PF_6]$, or dark green $[M_2(\mu-CO)(\mu-NO)(\eta-C_5R_5)_2][PF_6]$ (5; $M = Co$, $R = Me$) (82%), $\tilde{\nu}(CO)$ 1843, $\tilde{\nu}(NO)$ 1552 cm^{-1} , the more sterically demanding C_5Me_5 rings facilitating the decarbonylation of (4; $M = Co$, $R = Me$). Complexes (4) and (5) are direct analogues of (1) and (2) respectively with the low $\tilde{\nu}(NO)$ values revealing the preferential bridging of the nitrosyl groups.

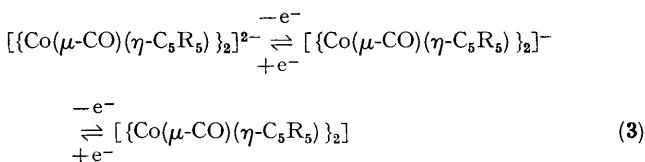
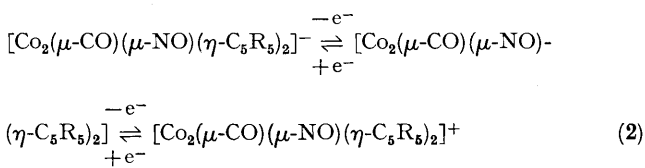
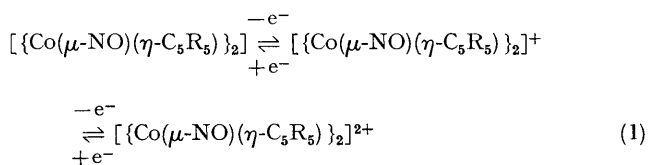


SCHEME. All reactions were performed in CH_2Cl_2 . Reagents: i, $[NO][PF_6]$; ii, $[M(CO)_2(\eta-C_5R_5)]$; iii, boiling CH_2Cl_2 ; iv, NO gas; v, $L = PPh_3$, cyclo-octene, etc.

The prolonged reaction of an excess of $[NO][PF_6]$ with $[Co(CO)_2(\eta-C_5H_5)]$ in CH_2Cl_2 gives the dark red-mauve complex $[\{ M(\mu-NO)(\eta-C_5R_5) \}_2][PF_6]$ (6; $M = Co$, $R = H$)

(42%), $\tilde{\nu}(NO)$ 1560 cm^{-1} , the paramagnetism of which is revealed by the 15-line e.s.r. spectrum [g_{av} 2.04, A_{iso} (^{59}Co) 42 G]. Complex (6) which can, in the case of the C_5Me_5 derivative, be made directly from (5) and NO gas in 90% yield, results from the reaction between (5) and $[NO]^+$. The formation of the complex $[\{ M(\mu-NO)(\eta-C_5R_5) \}_2][PF_6]$ (7; $M = Co$, $R = Me$), $\tilde{\nu}(NO)$ 1623 cm^{-1} , is followed by spontaneous reduction to (6; $M = Co$, $R = Me$), $\tilde{\nu}(NO)$ 1560 cm^{-1} , g_{av} 2.06, A_{iso} (^{59}Co) 39 G. Further evidence for the existence of the diamagnetic dication (7) is two-fold. First, cyclic voltammetry at a Pt electrode in CH_2Cl_2 shows that (6; $M = Co$, $R = Me$) undergoes reversible one-electron oxidation at 0.84 V (*vs.* a saturated calomel electrode); the high potential correlates with the ready reduction of (7; $M = Co$, $R = Me$). Secondly, although $[Rh(CO)_2(\eta-C_5H_5)]$ and $[NO][PF_6]$ yield only the red brown complex (4; $M = Rh$, $R = H$) (40%), $\tilde{\nu}(CO)$ 2074 and 2048, $\tilde{\nu}(NO)$ 1636 cm^{-1} , which is slowly decarbonylated to the dark blue (5; $M = Rh$, $R = H$), $\tilde{\nu}(CO)$ 1846, $\tilde{\nu}(NO)$ 1524 cm^{-1} , $[Rh(CO)_2(\eta-C_5Me_5)]$ affords the deep blue complex (7; $M = Rh$, $R = Me$) (55%), $\tilde{\nu}(NO)$ 1610 cm^{-1} .

Although the one-electron oxidation of $[\{ Co(NO)(\eta-C_5H_5) \}_2]$ and of $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5H_5)_2]$ has been detected by cyclic voltammetry,⁵ our results show the existence of the three-membered redox series in equation (1) and, by implication, the isoelectronic series in equations (2) and (3).



The synthetic potential of the binuclear complexes described is illustrated by the reactions of (4; $M = Rh$, $R = H$) with ligands ($L = PPh_3$, cyclo-octene, etc.) to give the complexes $[Rh(CO)_2(\eta-C_5H_5)]$ and $[Rh(NO)L(\eta-C_5H_5)]^+$ [$L =$ cyclo-octene, 93%, khaki crystals, $\tilde{\nu}(NO)$ 1845 cm^{-1}] (Scheme). Ethylene reacts similarly, but reversibly, in that partial evacuation of a CH_2Cl_2 solution of $[Rh(CO)_2(\eta-C_5H_5)]$ and $[Rh(NO)(C_2H_4)(\eta-C_5H_5)]^+$ leads to the regeneration of (4; $M = Rh$, $R = H$). The reversible formation of binuclear species, *via* nitrosyl-ligand bridge-terminal bond-

† Compounds for which yields are quoted have been isolated as solids and characterised by elemental analyses (C and H).

ing, is unprecedented and has clear implications for the reactions at dimetal centres.

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