Synthesis and Reactions of Cationic Rhodium Nitrosyl Complexes

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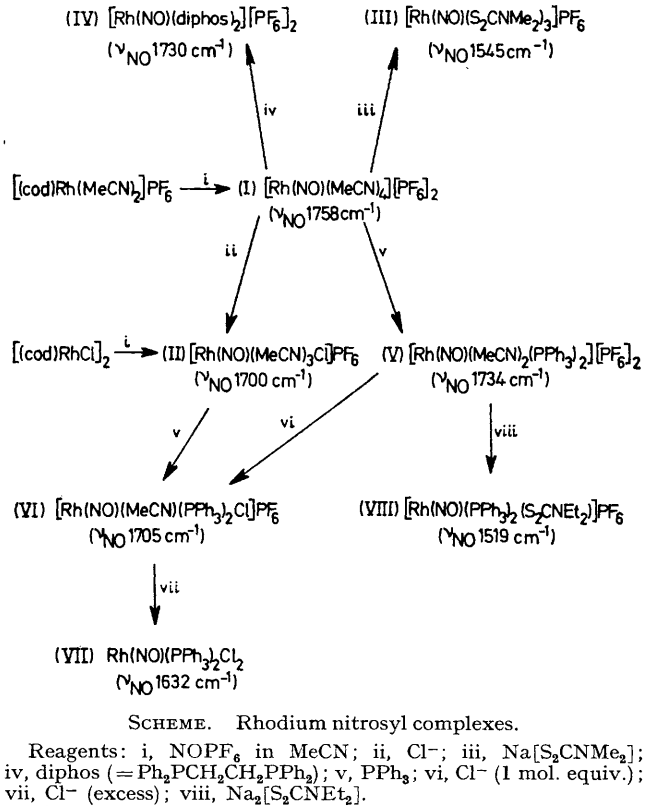
Summary The synthesis of the dication $[Rh(NO)(MeCN)_4]^{2+}$ and its reactions with uninegative and neutral ligands are described.

RECENTLY evidence has been presented for the ready interconversion of trigonal bipyramidal (linear NO) $[Co(NO)Cl_2L_2]$ (L = phosphine ligand) and the corresponding square pyramidal (bent NO) isomer.[1] An understanding of this kind of process, which involves both a change in geometry and in the formal oxidation state of the metal, is clearly important, particularly if catalytic reactions are to be developed based on this or related systems. With this in mind we have developed a synthesis of cationic five-co-ordinate rhodium nitrosyl complexes having readily displaceable ligands, which provides access to a range of new complexes of potential interest

Reaction of $[Rh(cod)(MeCN)_2]^+PF_6^-$ with $NOPF_6$ in MeCN, followed by precipitation with Et_2O, affords virtually quantitative yields of green crystalline (I)† [ν(CN) 2345m, 2325m; τ (CD_3CN) 7·33 (s)], which readily undergoes exchange reactions with CD_3CN, Bu^tCN, or PhCN. With anionic reagents, one or more acetonitrile ligands are displaced affording green (II) [ν(CN) 2335m, 2310m] with chloride anion, and dark red-brown (III) with excess of $Na[S_2CNMe_2]$. The species (II) may also be prepared from the reaction of $NOPF_6$ with either $[Rh(cod)Cl]_2$ or $[Rh(CO)_2Cl]_2$ in MeCN. Reaction of (I) with neutral phosphorus donor ligands results in either partial or complete acetonitrile displacement, yielding the green crystalline complexes (IV) and (V) [ν(CN) 2320m; τ (CD_3NO_2) 7·79 (s) and 2·10 (m)] with excess of PPh_3 (Scheme). Equimolar quantities of chloride anion react with (V) to give green crystals of (VI) [τ (CD_2Cl_2) 8·52 (s) and 2·64 (m)], which may also be obtained from (II) and PPh_3. An excess of chloride ion yields the known compound (VII). Treatment of (V) with $Na[S_2CNEt_2]$ gives yellow crystals of (VIII) [τ(CD_2Cl_2) 9·28 (t), 7·12 (q), and 2·62 (m)]. Interestingly, reaction of (V) with CO (10 atm.) leads to displacement of the nitrosyl ligand and the formation of $[Rh(CO)_2(PPh_3)_2]^+PF_6^-$.

It seems possible that (I) will have a square pyramidal (SP) structure, with a bent, axial nitrosyl group, since the nitrile ligands, with little or no π-accepting capacity, would be expected to force electron density on to the nitrogen atom of the NO ligand. Substitution by π-accepting



SCHEME. Rhodium nitrosyl complexes.

Reagents: i, $NOPF_6$ in MeCN; ii, Cl^-; iii, $Na[S_2CNMe_2]$; iv, diphos (= $Ph_2PCH_2CH_2PPh_2$); v, PPh_3; vi, Cl^- (1 mol. equiv.); vii, Cl^- (excess); viii, $Na_2[S_2CNEt_2]$.

All i.r. spectra in Nujol.

cod = cyclo-octa-1,5-diene.

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† All new compounds have satisfactory analyses and equivalent conductance values (in $MeNO_2$).

phosphorus ligands would then be expected to result in a change in geometry to the trigonal bipyramidal (TP) structure with an equatorial, linear nitrosyl ligand. However, a comparison of the nitrosyl stretching frequencies of (I) and (IV), while not a fully reliable criterion, suggests a linear metal-nitrosyl arrangement for both. The species $[Ru(NO)(diphos)_2]^+PF_6^-$, which is isoelectronic with (IV) has been shown to have a TP structure,[2] and moreover readily undergoes a Berry pseudo rotation process.[3] A similar process probably occurs more readily with (IV), since the proton decoupled ^{31}P FT n.m.r. spectrum (−80°) shows a single resonance at −52 p.p.m. (rel. to H_3PO_4) [d, $J(^{103}Rh-^{31}P)$ 117 Hz]. The spectrum (−80°) of (V) also shows a single resonance at −98 p.p.m. (rel. to H_3PO_4) [d, $J(^{103}Rh-^{31}P)$ 93 Hz].

The nitrosyl stretching frequency of (VIII), which is some 200 cm^{-1} lower than that of (V), strongly suggests the presence of a bent nitrosyl ligand in the former. The factors influencing the interchange between NO^+ and NO^- bonding in this system thus seem dependent on relatively minor changes of the remaining ligands.

The complex (III) is isoelectronic with $Ru(NO)(S_2CNEt_2)_3$ (ν_{NO} 1803 cm^{-1}), which has been shown to have an octahedral structure with a linear nitrosyl *trans* to one of the sulphur atoms of a bidentate sulphur ligand.[4] In contrast, the rhodium system (III) shows a nitrosyl stretch at 1545 cm^{-1} implying seven-co-ordination with a bent nitrosyl (NO^-) and bidentate sulphur ligands.

As indicated by the reactions shown in the Scheme the dication (I) has considerable synthetic potential. It is expected that variation of the ligands co-ordinated to rhodium should provide systems in which the relative stabilities of SP and TP geometries become comparable, thus allowing their interconversion to be studied.

(*Received*, 17*th April* 1974; *Com.* 436.)

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