Contribution from the Department of Chemistry Stanford University,[c]
Stanford, California, 94305 U.S.A. and Centro di Chimica e Tecnologia
dei Composti Organo-metallici degli elementi di transizione del C.N.R.,
Facoltà Chimica Industriale 40136 Bologna, Italy.[a]

Oxidative-Addition Reactions of d^{10} Nitrosyl Complexes

G. Dolcetti,[a] N. W. Hoffman,[b] and J. P. Collman[c]

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Oxidative addition reactions of complexes of the type $M(NO)L_3$ where M = Co, Rh, Ir, and L = tertiary phosphine are described. Nuclear magnetic resonance spectra of the starting complexes are consistent with C_{3v} pseudo-tetrahedral structure in solution. Infrared νNO frequencies for a range of nitrosyl complexes are discussed in terms of the nature of the NO ligand.

Introduction

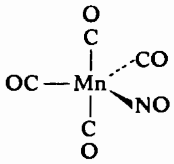
Our interest in oxidative-addition reactions of low-valent transition metal complexes led us to consider nitrosyl complexes. Since neutral d^{10} complexes such as PtL_4 and PdL_4 (L is tertiary phosphine) were known to undergo a large number of oxidative additions[1] we chose to study complexes of the type $M(NO)L_3$ (M = Co, Rh, Ir) which are isoelectronic with the above mentioned Pt and Pd compounds if the nitrosyl ligand is considered NO^+ in oxidation state formalism. After learning that Roper[2] was carrying on an extensive parallel study with $Ir(NO)(P(C_6H_5)_3)_3$ we have restricted our investigation to the rhodium and cobalt analogues.

More recently Stiddard[3] has reported oxidative addition reactions of a ruthenium nitrosyl, $RuCl(NO)(P(C_6H_5)_3)_2$.

On the basis of a series of recent precise X-ray diffraction studies[4] it is clear that the NO group is often found in either of two limiting oxidation states, NO^+ or NO^-[5], authough intermediate states[6] are occasionally found. Thus, structural ambiguity of the nitrosyl often renders reactions of these compounds more complex than those of carbonyl analogues.

Complexes exhibiting the NO^+ form see to be more common and are characterized by nearly linear M-N-O angles and comparatively short M-N bond lengths(4c,e,f,h,i,j) suggesting strong π-acidity. These complexes are often coordinatively saturated and the coordination geometry is that expected for the oxidation state of the metal calculated by considering NO as a unipositive ligand. Typically NO^+ complexes have carbonyl analogues of the same overall charge in which the central metal is in the next triad to the right. An example of this type of complex is provided by the saturated manganese (-I) complex **1**.(4c,e,h,k,l,m)

Complexes of the NO^- type are characterized by M-N-O angles approaching 120° and rather long M-N bonds(4a,d,b,i). These complexes are usually coordinatively unsaturated and typically the position *trans* to the NO^- ligand is unoccupied. The first precisely determined structure of this type is **2**(4a,b)) which can be considerated a pseudo-octahedral iridium(III) complex missing a ligand *trans* to NO. An example of a relatively rare saturated NO^- complex is given by **3**(4d) which exhibits the longest Co^{III}-Cl bond yet measured, illustrating the very strong *trans* labilizing effect of the NO^- group. This *trans* effect undoubtably accounts for the unsaturated nature of most NO^- complexes. The bent NO form has no analogy in CO complexes but these may be anticipated as excited states.



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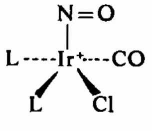
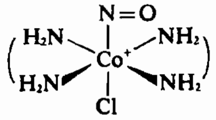


$L = P(C_6H_5)_3$

2



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[b] NDEA Graduate Fellowship 1967-70.
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b. C. A. Reed and W. R. Roper *Chem. Comm.*, 1459 (1969).
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i. C. G. Pierpont, D. G. van der Veer, W. Durland, and R. Eisenberg, *J. Am. Chem. Soc.*, *92*, 4760 (1970).
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k. C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Am. Chem. Soc.*, *93*, 3050 (1971).
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m. P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, *83*, 2593 (1961).
(5) The charges assigned to the two forms of the NO ligand are utilized for oxidation state formalism. The actual charge on N may vary considerably. A more realistic distinction between the two may be through designation of the hybridization of the two N atoms.
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The two limiting forms of the NO group cannot be unequivocally distinguished on the basis of the νNO frequencies for both limiting bond types. From these data it is apparent that whereas values for NO^+ are on the average higher than those for NO^-, the two ranges overlap (1890 to 1600 cm^{-1} for νNO^+ and 1720 to 1560 for νNO^-). The half-width of νNO bands in both forms are much broader than those of νCO[7], but at present the origin of this difference is not understood.

Results and Discussion

The tris-phosphine nitrosyls were prepared by the methods illustrated in eq. 1-6. The procedures used in eq. 1 and 4 are extensions of Heiber's methods,(8a,b) while that in eq. 5 is a modification of a synthesis by Levison and Robinson(8c).

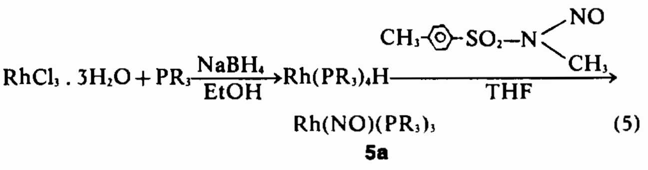
$$[CoCl(NO)_2]_2 + PR_3 \xrightarrow[THF]{Na(Hg)_x} \underset{\textbf{4a, b}}{Co(NO)(PR_3)_3} \qquad (1)$$

$$RhCl(P(C_6H_5)_3)_3 \xrightarrow[\substack{2)\ Na(Hg)_x \\ THF \\ P(C_6H_5)_3}]{1)\ NO,\ C_6H_6\ ^{8d}} \underset{\textbf{5a}}{Rh(NO)(P(C_6H_5)_3} \qquad (2)$$

$$MCl_3 . 3H_2O + P(C_6H_5)_3 + NO + Zn \xrightarrow{THF} M(NO)(P(C_6H_5)_3)_3 \qquad (3)$$

5a M=Rh
6 M=Ir

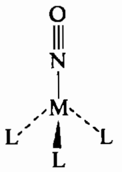
$$[RhCl(NO)_2]_x + PR_3 \xrightarrow[THF]{Na(Hg)_x} \underset{\textbf{5a, b, c, d}}{Rh(NO)(PR_3)_3} \qquad (4)$$



$$RhCl_3 . 3H_2O + PR_3 \xrightarrow[EtOH]{NaBH_4} Rh(PR_3)_4H \xrightarrow[THF]{CH_3\text{-}C_6H_4\text{-}SO_2\text{-}N(NO)CH_3} \underset{\textbf{5a}}{Rh(NO)(PR_3)_3} \qquad (5)$$

$$IrCl(N_2)(P(C_6H_5)_3)_2 \xrightarrow[\substack{2)\ Na(Hg)_x \\ P(C_6H_5)_3}]{1)\ NO} \underset{\textbf{6}}{Ir(NO)(P(C_6H_5)_3)_3} \qquad (6)$$

Each synthesis except eq. 5 depends upon the introduction of the NO ligand into a higher oxidation state form followed by reduction of chloride derivative in the presence of the appropriate phosphine. Each of the complexes, **4a,b**, **5a,b,c,d** and **6** is provisionally assigned the C_{3v} structure shown. An X-ray structure[9] of the iridium nitrosyl **6** has shown it to have this structure and the n.m.r. results discussed below are consistent with this formulation. An alternative bent NO^- structure would be expected for a square planar form, resulting in severe steric repulsions between the three bulky tertiary phospines. The νNO frequencies (Table II) decrease on descending the triad, Co>Rh>Ir. The similar solution and solid state i.r. spectra suggest the same structural form in each phase.



4 = M=Co, **a** $L=P(C_6H_5)_3$; **b** $L=P(CH_3)(C_6H_5)_2$
5 = M=Rh, **a** $L=P(C_6H_5)_3$; **b** $L=P(CH_3)(C_6H_5)_2$;
c $L=(p\text{—}CH_3C_6H_4)_3P$; **d** $L=(p\text{—}F\text{—}C_6H_4)_3P$
6 = M=Ir; $L=P(C_6H_5)_3$

In view of the extensive dissociation of the similar d^{10} complexes ML_4 (M = Pd or Pt and L = R_3 P) and the greater kinetic reactivity of the unsaturated species[10] it seemed important to determine the degree of dissociation for these mono-nitrosyl analogues. Osmometric molecular weight measurement on the relatively air-stable iridium nitrosyl **6** show it to be monomeric; however, we were unable to determine a molecular weight for the rhodium complex **5a** due to its sensitivity towards O_2. ^1H and ^{19}F nuclear magnetic resonance spectra of degassed solutions of **4b**, **5b**, and **5d** failed to detect the presence of the uncoordinated phosphines $P(CH_3)(C_6H_5)_2$ and $(p\text{-}F\text{-}C_6H_4)_3P$ within the limits of our measurements. Added portions of these uncoordinated ligands resulted in n.m.r. spectra identical with simple addition of the two isolated spectra. The failure of added free phosphine to perturb the spectrum of the coordinated phosphine indicates ligand exchange if any is slow on the n.m.r. time scale and that ligand dissociation does not take place.

The methyl resonance in the spectra of **5a,b,d, 4b** at 25° occurs as ill-resolved multiplets. Further broadening of these signals takes place as the temperature is lowered. Upon raising the temperature these signals sharpen to well resolved doublets (at 107° for the cobalt complex **4b**, 80° for the rhodium analogue **5b**). We interpret these data as resulting from restricted rotation about the M-P bond at the lower temperatures which produces magnetically inequivalent methyl groups; more rapid rotation at high temperatures equilibrates these methyl groups on the n.m.r. time scale. The longer Rh-P bonds would be expected to afford a lower rotational barrier.

The observation of a simple well-resolved methyl doublet at higher temperature is consistent with the C_{3v} symmetry (tetrahedral coordination geometry) assigned to those complexes and expected from an NO^+-M(-I) oxidation state formalism.[11]

The rhodium nitrosyls **5a-d** are moderately active

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(7) A. Poletti, A. Foffani, R. Cataliotti, *Spectrochimica Acta*, *26A*, 1063 (1970).

(8) a. W. Hieber and K. Heinicke, *Z. Anorg. Allgem. Chem.*, *316*, 305 (1962).
b. W. Hieber and K. Heinicke, *Z. Anorg. Allgem. Chem.*, *316*, 321 (1962).
c. J. J. Levison and S. O. Robinson, *Chem. Ind.*, 1514 (1969).
d. $RhCl(PPh_3)_3$ reacts with NO to form $RhCl(NO)_2(NO)(PPh_3)_2$ (identified by W. B. Hughes, *Chem. Comm.*, 1126 (1969)) which is reduced by the amalgam.

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b. J. P. Birk, J. Halpern and A. L. Pickard, *Inorg. Chem.*, *7*, 2672 (1968).

(11) A very similar result for $Co(NO)(CO)(PMe_2Ph)_2$ was recently reported by R. J. Mawby, G. Wright and D. Ewing, *J. Organometal. Chem.*, *23*, 545 (1970).

Table I. Selected metal-nitrogen, nitrogen-oxygen bond lengths, metal-nitrogen-oxygen bond angles, and infrared nitrosyl stretching frequencies ($L=P(C_6H_5)_3$ en = ethylenediamine, diphos = 1,2-diphenylphosphinoethane).

Compound	M—N Å	M—N—O deg.	N—O Å	νNO cm^{-1}	Formulation
$(C_6H_5)_3MoNO$	1.751 [a]	179.2	1.207	1610 [a]	NO^+
$MnNO(CO)_4$	1.797 [b]	180	1.152	1725 [c]	NO^+
$MnNO(CO)_3L$	1.78 [d]	177.9	1.15	1710 [e]	NO^+
$MnNO(CO)_2L_2$	1.73 [f]	178.0	1.18	1661 [g]	NO^+
$[CoNO(NH_3)_5]Cl_2$	1.87 [h]	119.0	n.a.	1610 [i]	NO^-
$[CoCl(NO)(en)_2]^+ClO_4^-$	1.813 [j]	121.3	1.14	1635 [k]	NO^-
$Ni(N_3)(NO)L_2$	1.69 [l]	153.0	1.16	1710 [l]	NO^+
$[RuCl(NO)_2L_2]PF_6$	1.859 [m]	136.0	1.170	1687 [m]	NO^-
$[RuCl(NO)_2L_2]PF_6$	1.738 [m]	180.0	1.162	1845 [m]	NO^+
$RuH(NO)L_3$	1.795 [n]	176	1.180	1640 [n]	NO^+
$[Ru(NO)(diphos)_2]^+$	1.735 [n]	174	1.197	1673 [n]	NO^+
$[IrCl(NO)(CO)L_2]BF_4$	1.972 [o]	124.1	1.16	1680 [o]	NO^-
$[IrI(NO)(CO)L_2]BF_4 . C_6H_6$	1.89 [p]	125	1.17	1720 [p]	NO^-
$IrNOL_3$	1.67 [q]	180	1.24	1600 [r]	NO^+
$[IrH(NO)L_3]ClO_4$	1.68 [s]	175	1.21	1673 [t]	NO^+
$IrI(CH_3)NOL_2$	1.91 [u]	120	1.23	1525 [t]	NO^-
$IrCl_2NOL_2$	1.94 [v]	123	1.03	1560 [t]	NO^-
$OsCl_2(HgCl)NOL_2$	1.79 [w]	178	1.03	1820 [w]	NO^+

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Table II. Infrared stretching frequencies for nitrosyl compplexes (as nujol mulls).

Compound		νNO cm^{-1}	Other bands cm^{-1}	Reference
NO (gas)		1876		32
$NO^+PF_6^-$		2220		32
$Mn(NO)(CO)_4$	*1*	1725s	ν(CO) 2095m, 2019s, 1972s	4m
$[IrCl(NO)(CO)(P(C_6H_5)_3)_2]^+PF_6^-$	*2*	1680vs	ν(CO) 2050vs	4a,b
$[CoCl(NO)en_2]^+ClO_4^-$	*3*	1611vs		4d
$CoNO(P(C_6H_5)_3)_3$	*4a*	1640vs		33
$CoNO(P(C_6H_5)_2(CH_3))_3$	*4b*	1630vs		33
$RhNO(P(C_6H_5)_3)_3$	*5a*	1612vs		12a
$RhNO(P(CH_3)(C_6H_5)_2)_3$	*5b*	1570vs [a]		this work
$RhNO(P(p-CH_3C_6H_4)_3)_3$	*5c*	1600vs [a]		this work
$RhNO(P(p-FC_6H_4)_3)_3$	*5d*	1630vs [a]		this work
$IrNO(P(C_6H_5)_3)_3$	*6*	1600vs		31
$RhNO[(CH_3-C(CH_2P(C_6H_5)_2)_3]$	*7*	1590vs [a]		this work
$RhNO(CO)(P(C_6H_5)_3)_2$	*8*	1670vs	ν(CO) 1970vs	33
$RhCl_2(NO)(P(C_6H_5)_3)_2$	*9*	1630vs [a]		this work
$RhCl_3(NH_2OH)(P(C_6H_5)_3)_2$	*10a*		[a] ν(N-H) 3280w, 3230w	this work
$RhCl_3(ND_2OD)(P(C_6H_5)_3)_2$	*10b*		[a] ν(N-D) 2460w, 2380w	this work
$IrCl_2(NO)(P(C_6H_5)_3)_2$	*11*	1560vs		2a
$CoCl_2NO(P(C_6H_5)_3)_2$	*12*	1640s, 1725m		17
$Co(NO)(CO)(P(C_6H_5)_3)_2$	*15*	1717vs	ν(CO) 1932vs	33
$CoCi(NO)_2(P(C_6H_5)_3)_2$	*17*	1776m, 1815m		20
$CoI_2NO(P(C_6H_5)_3)_2$	*18*	1775vs [a]		this work
$CoI(NO)_2(P(C_6H_5)_3)_2$	*19*	1775m, 1815m		33
$[Rh(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-$	*22a*	1720s, 1760s		this work
$[Ir(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-$	*22b*	1700s, 1760s [a]		this work
$Ir(NO)(CO)(P(C_6H_5)_3)_2$	*25*	1660s, 1645vs	ν(CO) 1950vs, 1920s	15
$RhNO)(P(C_6H_5)_3)_2$(maleic anhydride)	*26*	1630s	ν(CO) 1800s, 1730s	23
$Ir(NO)(P(C_6H_5)_3)_2$(maleic anhlydride)	*27*	1672s	ν(CO) 1813s. 1750s	23

[a] KBr pellets

homogeneous catalysts[12] for the hydrogenation of terminal olefins at 25° and 1 atm H_2, although the corresponding iridium and cobalt complexes are not effective catalysts under these mild conditions. The iridium nitrosyl **6** does exhibit catalytic at 85° and 4 atm, but the cobalt complex **4a** is inactive even under severe conditions (50° and 2000 p.s.i. H_2). H_2 at 1 atm produces no detectable change on the infrared spectra of **5a** or **6**, so it appears likely that the catalytic-

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b. K. C. Dewhirst, *U. S. Patent*, 3,366,646 (1968).

ally active dihydride species is formed reversibly in very low concentration. It is possible that the relatively limited catalytic activity of these rhodium nitrosyls (and the still smaller activity of the iridium nitrosyl) may be due to the very slight degree of dissociation of phosphine to form a three-coordinate unsaturated species. That phosphine ligand dissociation must occur during some part of the catalytic cycle is suggested by inhibition of the reaction by added phosphine and by inactivity of the related complex $[Rh(NO)P_3]$,**7**, (where P_3 is the tripodal ligand $CH_3\text{-}C(CH_2P(C_6H_5)_2)_3$) which must maintain tetrahedral geometry due to the steric constraint of the tripodal phosphine. It is also interesting that **7** does not react with CO, whereas the triphenylphosphine analogue **5a** forms a monocarbonyl derivative **8** (eq. 7):

$$\underset{\textbf{5a}}{Rh(NO)(P(C_6H_5)_3)_3} + CO \longrightarrow \underset{\textbf{8}}{Rh(NO)(CO)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 \qquad (7)$$

Oxidative addition of H_2 is an essential step in catalytic hydrogenation and only unsaturated metal complexes seem to undergo this reaction in the absence of base. Until recently, d^{10} complexes were believed inert to H_2 (due to completely filled metal d orbitals unavailable to attack by H_2 $1s\sigma$ electrons), and no definite examples of oxidative addition of H_2 by d^{10} complexes were known. Muetterties et al[13] have shown that $Pt(P(CH_3)_3)_3$ reacts with H_2 to form the five-coordinate dihydride $H_2Pt(P(CH_3)_3)_3$. Thus, it appears that the nitrosyls may react with H_2 via dissociation to a reactive three-coordinate d^{10} species rather than necessarily through a nitrosyl valence tautomer $M^I(NO^-)L_3$, an unsaturated four-coordinate d^8 complex.

Catalytic homogeneous hydrogenation properties of the d^{10} nitrosyl series are best illustrated by the reactions of the rhodium nitrosyls **5a-d**. Reductions were carried out in dichloromethane, where isomerization of the substrate was negligible (unlike in benzene and tetrahydrofuran where a large degree of isomerization was noted). Catalytic activity for $RhNOL_3$ shows the following dependence on L: $(p\text{-}CH_3C_6H_4)_3P > P(C_6H_5)_3 > (p\text{-}FC_6H_4)_3P > P(CH_3)(C_6H_5)_2$. Substrates are reduced by $Rh(NO)(P(C_6H_5)_3)_3$ in the order alk-1-yne > alk-2-yne > alk-1-ene > exomethylene > cycloalkene > *cis*-alk-2-ene > *trans*-alk-2-ene > tri-substituted olefin ≫ tetra-substituted olefin. Ethylene, propylene, and allene are easily reduced at 1 atm H_2 and 25° Non-conjugated non-chelating dienes are reduced at the same rate as monoaleknes. Conjugated dienes and strongly bonding chelating dienes are generally reduced at significantly lower rates or not at all (probably due to blocking of a coordination site needed for oxidative addition of H_2). Isoprene, 1,3-butadiene, and 2,4-hexadiene are only slowly reduced, forming all possible monoene isomers. 1,5-cyclooctadiene cannot be reduced even at 30° and 8 atm H_2; it also inhibits the hydrogenation of cyclohexene. For 1,3-cyclooctadiene and norbornadiene, however, hydrogenation proceeds at rates nearly those of terminal olefins; the dienes are not isomerized and are reduced faster than the monoenes produced in the first stage of hydrogenation.

The stereochemistry of $Rh(NO)(P(C_6H_5)_3)_3$ - catalyzed hydrogenation of olefins has been elucidated by utilizing Wilkinson's adaptation[14a] of the work of Childs and Bloch[14b]. With an average 25 p.s.i.g. D_2 in dichloromethane, the deuteration of dimethyl maleate was taken to completion. Since the relative rates of (A) reduction of maleate to succinate, (B) isomerization of maleate to fumarate, and (C) reduction of fumarate to succinate were determined in previous experiments with the nitrosyls catalyst as $(A);(B):(C) \approx 150:1:8$, calculations showed that products resulting from a path through fumarate would be insignificant within the accuracy of the infrared measurements. The product succinate was purified by prepative G.L.C.; mass spectroscopy showed it to be completely dideuterated. Infrared studies in CS_2 showed the product to be $\sim 90\%$ *meso*-d_2-dimethylsuccinate (formed by *cis*-addition of D_2 to maleate). Thus, it appears that reduction of olefin occurs in two steps (hydride transfers) and that the second step usually occurs before the Rh-C bond can rotate; otherwise the *trans*-addition D,L product would be formed to a greater extent.

Two other experiments have also substantiated the stereospecificity of the nitrosyl hydrogenation catalysis. Reduction of cyclohexene with D_2 yields only d_2-cyclohexane. Hydrogenation of 2-hexyne produces $\geqslant 99\%$ *cis*-2-hexene (G.L.C. analysis) which would be formed by *cis*-addition of H_2 to the alkyne.

The rhodium nitrosyl **5a** in the absence of H_2 and O_2 was shown not to catalyze the isomerization of terminal olefins. On slight exposure to air, however, a solution of **5a** in CH_2Cl_2 slowly converted an excess of 1-hexene into its internal isomers, with phosphine oxide detected by infrared. Presumably oxidation of a phosphine gives the complex a free site with which to coordinate olefin for isomerization via a π-allyl-hydride intermediate.

Treatment of the rhodium nitrosyl **5a** with dry HCl affords different products depending upon the conditions. Reaction of **5a** with two equivalents of HCl in benzene yields the dichloride **9** (eq. 8) whereas an excess of dry HCl in CH_2Cl_2 affords a product which we now believe to be a hydroxylamine complex **10** (eq. 9). Earlier we proposed the trichloride as a complex of nitroxyl[12a] but its similarity to the corresponding iridium hydroxylamine complex recently characterized by Roper[15] has led us to reformulate the rhodium trichloride as **10**; a product previously formulated as $Rh(P(C_6H_5)_3)_2(HNO)Cl_3$ whose infrared contained a strong nitrosyl stretching frequency at 1630 cm^{-1} was separated into two complexes (by chromatography on silica gel) whose infrared spectra were identical respectively to those of the dichloride **9** and the NH_2OH complex **10a**. In each case elemental analyses and i.r. spectra are consistent with the suggested structures, with the NH_2OH ligand characterized by N-H and O-H stretching frequencies

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[13] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.*, *93*, 3543 (1971).

[14] a. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1711 (1966).
b. C. R. Childs and K. Bloch, *J. Org. Chem.*, *26*, 1630 (1961).

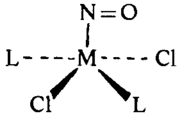
[15] C. A. Reed and W. R. Roper, *J. Chem. Soc.* (*A*), 3054 (1970).

(Table II). The dichloride was also prepared by chlorination of **5a**.

$$\underset{\mathbf{5a}}{Rh(NO)(P(C_6H_5)_3)_3} + 2HCl \xrightarrow{C_6H_6} \underset{\mathbf{9}}{RhCl_2(NO)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 + H_2 \tag{8}$$

$$\underset{\mathbf{5a}}{Rh(NO)(P(C_6H_5)_3)_3} + 3HCl \longrightarrow \underset{\substack{\mathbf{10a}\\ \mathbf{b}\ (NH_2OD)}}{RhCl_3(NH_2OH)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 \tag{9}$$

The dichloride is assigned a bent NO^- structure **9** like the analogous iridium complex **11** (whose structure has been determined by X-ray diffraction) in spite of the 70 cm^{-1} difference between their νNO frequencies (1630 cm^{-1} for Rh and 1560 cm^{-1} for Ir).



$L = P(C_6H_5)_3$

9 M=Rh; **11** M=Ir

The cobalt nitrosyl **4a** reacts with dry HCl to form a mixture of the dichloro-nitrosyl **12** and the cobalt(II) dichloride **13** (eq. 10). When excess HCl is employed, **13** is the only product. Complexes such as **12** have been prepared by treating $[CoCl_2L_2]$ with NO^{16}. The presence of two νNO bands in **12** (Table II) suggests two structures in conformational equilibrium-one having a bent NO^- similar to **9** and the other with a linear $NO^{+\ 16,17}$.

$$\underset{\mathbf{4a}}{Co(NO)(P(C_6H_5)_3)_3} + HCl \longrightarrow \underset{\mathbf{12}}{CoCl_2(NO)(P(C_6H_5)_3)_2} + \underset{\mathbf{13}}{CoCl_2P(C_6H_5)_3)_2} \tag{10}$$

The rhodium and cobalt nitrosyls **5a** and **4a** react differently with benzoyl chloride (eq. 11 and 12). The very stable rhodium(I) carbonyl **14** is formed from the rhodium nitrosyl upon heating or prolonged reaction. Apparently nitrosobenzene is eliminated but we were unable to detect this reactive substance. An intermediate benzoyl chloride adduct was detected in the i.r. spectrum during the initial stage of the reaction.[12a] The cobalt nitrosyl takes a different path forming the cobalt(I) nitrosvl carbonyl **15** and eliminating chlorobenzene which we detected by G.I.C. analysis.

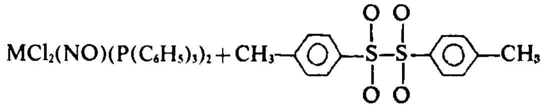
$$\underset{\mathbf{5a}}{Rh(NO)(P(C_6H_5)_3)_3} + C_6H_5COCl \longrightarrow \underset{\mathbf{14}}{RhCl(CO)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 + C_6H_5NO \tag{11}$$

$$\underset{\mathbf{4a}}{Co(NO)(P(C_6H_5)_3)_3} + C_5H_5COCl \longrightarrow \underset{\mathbf{15}}{Co(NO)(CO)(P(C_6H_5)_3)_2} + C_6H_5Cl + P(C_6H_5)_3 \tag{12}$$

All three nitrosyls, **5a**, **6** and **4a**, react rapidly with p-toluenesulfonyl chloride (eq. 13 and 14). But different types of products **9, 11,** and **13** respectively are formed, with rhodium and iridium retaining but cobalt losing the NO ligand.

In each case two moles of sulfonyl chloride are consumed but neither SO_2 nor a sulfinate complex could be detected. Either product would be expected on the basis of oxidative additions of aryl sulfonyl chlorides described earlier.[18,19] In view of Alper's report[20] that a disulfone is formed from the reaction of $Fe(CO)_5$ and aryl sulfonyl chlorides, we looked for and found the disulfone **16** from reaction of the rhodium and iridium nitrosyls **5a** and **6** (eq. 13). Whether this reaction involves two successive oxidative additions, d^{10} to d^8 to d^6, followed by a reductive elimination or some free radical process is unclear.

$$\underset{\mathbf{5a}\ M=Rh;\ \mathbf{6}\ M=Ir}{M(NO)(P(C_6H_5)_3)_3} + p\text{—}CH_3C_6H_4SO_2Cl \longrightarrow$$



$MCl_2(NO)(P(C_6H_5)_3)_2 + $ **16** (13)

9 M=Rh; **11** M=Ir

By analogy with the iridium and rhodium reactions we expected to find the dichloro nitrosyl **12** from similar reaction of the cobalt complex **4a**. However the cobalt(II) dichloride **13** and the dinitrosyl monochloride **17** were isolated (eq. 14). The latter could have arisen from a disproportionation of the expected product **12** (sec eq. 16).

$$\underset{\mathbf{4a}}{Co(NO)(P(C_6H_5)_3)_3} + p\text{—}CH_3C_5H_4SO_2Cl \longrightarrow \underset{\mathbf{13}}{CoCl_2(P(C_6H_6)_3)_2} + \underset{\mathbf{17}}{CoCl(NO)_2(P(C_6H_5)_3)_2} \tag{14}$$

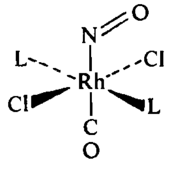
Both the rhodium and cobalt nitrosyls **5a** and **4a** react with mercuric iodide to form the diiodonitrosyls and elemental mercury. The reaction with cobalt is illustrated (eq. 15). The diodide, **18**, which can also be prepared by direct iodination, is unstable in polar solvents and forms the known dinitrosyl **19**[(8a)] and the cobalt(II) diiodide 20 (eq. 16). The stoichiometry of this reactions is not clear.

$$\underset{\mathbf{4a}}{Co(NO)(P(C_6H_5)_3)_3} + I_2(\text{or } HgI_2) \rightarrow \underset{\mathbf{18}}{CoI_2(NO)(P(C_6H_5)_3)_2} \tag{15}$$

$$\underset{\mathbf{18}}{CoI_2(NO)(P(C_6H_5)_3)_2} \xrightarrow{CH_3OH} \underset{\mathbf{19}}{CoI(NO)_2(P(C_6H_5)_3)_2} + \underset{\mathbf{20}}{CoI_2(P(C_6H_5)_3)_2} \tag{16}$$

In an earlier communication[(17)], we reported that the rhodium dichloronitrosyl **9** reacts with CO to form a six-coordinate Rh^{III} complex **21** (eq. 17) in

$$\underset{\mathbf{9}}{RhCl_2NO(P(C_6H_5)_3)_2} + CO \longrightarrow$$



(17)

21, $L = P(C_6H_5)_3$

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[16] G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

[17] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, 93, 1788 (1971).

which the nitrosyl stretching frequency remains identical to that of **9**, a rather surprising result. Further investigation of the reaction of various M(NO)-L_2X_2 complexes (M=Rh or Ir, L=tertiary phosphine, X=halide) with 1 atm CO at 25° has indicated that **21** is incorrectly formulated and that the reaction is much more complicated than simple addition of CO. $IrI_2(NO)(P(C_6H_5)_3)_2$ reacts rapidly with CO in dichloromethane forming an orange solution with four bands in the terminal carbonyl stretching region but none in the nitrosyl. $RhCl_2NO(P(CH_3)(C_6H_5)_2)_2$ reacts less rapidly to produce a solution which has four bands in the terminal carbonyl stretching region plus one in the bridging carbonyl region (appearing later in the course of the reaction than the terminal bands) and a significantly diminished nitrosyl stretching band unchanged in position. Further research is being conducted on the reactions of CO with this series of dihalonitrosyls and will be published separately.

The nitrosonium cation is capable of acting as a two electron oxidant by coordinating with a metal in the NO^- form. An example is the formation of **2** from addition of $NO^+PF_6^-$ to the iridium(I) carbonyl(4a). Eisenberg(4i) recently used this reaction to prepare $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-$ in which the two nitrosyls are found in the two limiting (NO^+ and NO^-) bond forms.

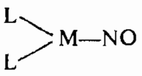
Correspondingly we treated the rhodium and iridium nitrosyls **5a** and **6** with $NO^+PF_6^-$. In each case a phosphine was replaced by NO affording the cationic bis nitrosyls **22a** and **22b** (eq. 18). The iridium dinitrosyl **22b** is a known substance prepared differently[21,22] by Angoletta and characterized as the perchlorate by an X-ray diffraction study(6) which revealed two equivalent NO groups with Ir-N-O angles of 164° and a coordination geometry intermediate between tetrahedral and planar. Because of the similarity between the i.r. spectra of **22a** and **22b** it seems likely that they have similar structure. Starting from the nitrosyl carbonyl **23**, the dinitrosyl cation **22b** is formed in a similar reaction except that CO is replaced (eq. 19).

The less basic complexes $MI_2(NO)(P(C_6H_5)_3)_2$ (M = Rh, Ir) fail to react with $NO^+PF_6^-$ under the same conditions, in spite of the presence of a latent coordination site.

$$\underset{\mathbf{5a}\ M=Rh;\ \mathbf{6}\ M=Ir}{M(NO)(P(C_6H_5)_3)_3} + NO^+PF_6^- \longrightarrow \underset{\mathbf{22a}\ M=Rh;\ \mathbf{b}\ M=Ir}{[M(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-} + P(C_6H_5)_3 \qquad (18)$$

$$\underset{\mathbf{23}}{Ir(NO)(CO)(P(C_6H_5)_3)_2} + NO^+PF_6^- \longrightarrow \underset{\mathbf{22b}}{[Ir(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-} + CO \qquad (19)$$

To obtain the theoretically more reactive unsaturated d^{10} nitrosyl **24a, b** *in situ*, several synthetic routes to complexes **25 a, b** containing a readily dissociated ligand or easily reduced olefin or alkyne were explored. Reaction of the nitrosyl-carbonyl complexes **8** and **23** with pyridine, C_2H_4, and CH_3CN gave either no reaction or decomposition.



$M(NO)L_2Z$

24 $L=P(C_6H_5)_3$
a = Rh
b = Ir

25 $L=P(C_6H_5)_3$
a = Rh, **b** = Ir
Z = labile ligand or easily reduced unsaturated ligand

$$M(NO)(CO)(P(C_6H_5)_3)_2$$
8 M=Rh
23 M=Ir

Reduction of the dihalonitrosyls $RhX_2(NO)(P(C_6H_5)_3)_2$ and $IrX_2(NO)(P(C_6H_5)_3)_2$ (X = Cl or I) with various reducing agents ($LiAlH_4$, Zn, $NaBH_4$, Mg, Redal) in the presence of various Z also failed to produce any desired product. Reaction of the rhodium dichloronitrosyl **9** with diisobutylaluminum hydride in the presence of added triphenylphosphine did not give the desired product but instead a dark red crystalline solid identified by its infrared spectrum as $RhCl(P(C_6H_5)_3)_3$. With sodium amalgam in THF, however, the dihalonitrosyls were converted almost quantitatively to the saturated d^{10} complexes **5a** and **6** in the presence of a slight excess of triphenylphosphine (eq. 20).

$$MX_2(NO)(P(C_6H_5)_3)_2 \xrightarrow[P(C_6H_5)_3]{Na/Hg,\ THF} \underset{\substack{\mathbf{5a}\ M=Rh \\ \mathbf{6}\ \ M=Ir}}{M(NO)(P(C_6H_5)_3)_3} + NaX \qquad (20)$$

In the presence of $Z \neq P(C_6H_5)_3$ the sodium amalgam reduction produced only the the tris-phosphine complexes **5a** and **6** (for $Z=C_2H_4$, $C_6H_5 \equiv CC_6H_5$, C_5H_5N, CH_3CN); for Z=CO (1 atm), a yellow product with no nitrosyl stretch but three carbonyl stretching frequencies in the 1990-1900 cm^{-1} range was isolated but not characterized further. Reaction of the rhodium dihalonitrosyls with H_2 (8 atm) in tetrahydrofuran at 60° in the presence of base (K_2CO_3 or $N(C_2H_5)_3$) resulted in dissolution of the relatively insoluble dihalonitrosyls to give dark blood-red solutions from which solid $Rh(NO)(P(C_6H_5)_3)_3$, **5a**, could be isolated in moderate yields; carrying out the reaction in the presence of excess triphenylphosphine gave quantitative yields of **5a** (eq. 21).

$$\underset{\mathbf{9}}{RhCl_2NO(P(C_6H_5)_3)_2} + P(C_6H_5)_3 + H_2 + 2K_2CO_3 \xrightarrow{THF} \underset{\mathbf{5a}}{Rh(NO)(P(C_6H_5)_3)_3} + 2KHCO_3 + 2KCl \qquad (21)$$

Carrying out the reduction with H_2 and base in the presence of a large excess of dimethyl maleate or diphenylacetylene formed only **5a** in moderate yield, as did exposure of the hydrogenated solution (with no added Z) to 8 atm C_2H_4. The analogous reduction with H_2 pressure

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(18) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, *88*, 180 (1966).
(19) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, *45*, 301 (1967).
(20) H. Alper, *Tetrahedron Letters*, 1239 (1969).
(21) M. Angoletta, *Gazz. Chim. Ital.*, *92*, 811 (1962).
(22) a. M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, *93*, 1584 (1963).
b. L. Malatesta, M. Angoletta and G. Caglio, *Angew. Chem.*, *75*, 1103 (1963).

and base occurred somewhat differently for $IrI_2(NO)(P(C_6H_5)_3)_2$ plus excess phosphine, forming a small amount of Ir(–I) nitrosyl but primarily a yellow solid with a band of medium-strong intensity at 1750 cm^{-1} in the infrared. Reaction of the maleic anhydride complexes **26** and **27** (prepared by simple ligand exchange as reported by Cenini *et al*[23]) with H_2 (4 atm) for five hours in dichloromethane at 25° followed by addition of 1-decene with stirring at 4 atm H_2 produced only very slow reduction of 1-decene (much slower than that catalyzed by the saturated rhodium nitrosyl **5a**); the iridium maleic anhydride complex **27** was found to be approximately five times as active as its rhodium analogue.

$M(NO)(P(C_6H_5)_3)_2$(maleic anhydride)
26 M = Rh
27 M = Ir

Use of the unsaturated species **24a, b** theoretically obtained by reduction of the dihalonitrosyl *in situ* failed to produce highly active homogeneous systems for reduction of terminal olefins. 1-decene was rapidly reduced under 1 atm H_2 over a slurry of reduced dihalonitrosyl $RhCl_2(NO)L_2$ (L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, or $P(n\text{-}C_4H_9)_3$) and sodium amalgam, but catalytic activity was reduced to levels comparable to that of **5a** when the supernatant solution was filtered under an inert atmosphere to remove any rhodium metal formed in the amalgam reduction. The similarly reduced iridium solution after filtration was a moderately active catalyst for reduction of terminal olefins at 25°, in marked contrast with the saturated nitrosyl **6** which is inactive under these conditions. Use of the H_2 plus base reducing system for rhodium dichloronitrosyls formed a solution only moderately active for catalytic hydrogenation; a nitrosyl species was demonstrated to be present by solution infrared of reduced $RhCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ showing ν(N-O) at 1605 cm^{-1}.

The results reported herein illustrate the capacity of nitrosyl complexes to undergo oxidation addition. The lack of dissociation of complexes of the type $M)NO)L_3$, **4-6** may account for the decreased reactivity of these substances relative to $\mathbf{d}^{10}$ complexes such as $Pt(P(C_6H_5)_3)_4$. Their reactivity towards oxidative addition follows the order Ir>Rh>Co expected on the basis of electronic promotion energies. Oxidized cobalt nitrosyls are unstable towards disproportionation, and the products isolated from reactions of cobalt(–I) nitrosyls may not be the initial ones formed by oxidative addition. Lack of an adequate single experimental method for distinguishing the NO bond types makes structural assignments of the product NO complexes difficult in the absence of X-ray diffraction studies.

Experimental

Equipment and general techniques. Volatile air-sensitive materials were handled on a preparative vacuum line equipped with mercury float valves. Nonvolatile air-sensitive substances were handled in a HE-43-2 Vac Atmosphere inert atmosphere chamber. All reactions described in this paper were performed under nitrogen or argon unless otherwise specified. Fischer-Porter bottles were used for all pressure reactions. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer and the solid samples were run as KBr pellets.

The analyses were determined by the microanalysis laboratory of the Chemistry Department, Stanford University.

N.m.r. spectra - Proton n.m.r. spectra were obtained with a Varian A-60 or Viaran HA-100 spectrometer equipped with variable temperature apparatus. $RhNO(P(CH_3)(C_6H_5)_2)_3$ and $RhNO(P(p\text{-}FC_6H_4)_3)_3$ samples with $\mathbf{d}_8$-THF as solvent were prepared on the vacuum line. Solutions of $CoNO(P(CH_3)(C_6H_5)_2)_3$ in chlorobenzene were prepared in the inert atmosphere chamber and then sealed under argon. TMS was used as internal standard in the proton spectra.

The ^{19}F spectra were obtained at 49.1 mcps using a Varian HA-100 spectrometer; hexafluorobenzene was used as internal reference and the chemical shifts were computed by the Graham method(24).

Hydrogenation experiments. - Hydrogenation reactions were run in Fischer-Porter bottles at 25° under 15 psig H_2 unless otherwise specified. The amount of catalyst used was 0.05 mmole and concentration of olefin was 16 m*M* in dichloromethane. The olefins were purified by passage through silica gel or neutral alumina columns to eliminate any peroxides present and were degassed with argon before use.

Solvents and reagents. - All solvents were reagent grade and were dried over appropriate reagents and distilled under nitrogen or argon. Solvents were degassed prior to use.

Nitric oxide was Matheson Gas commercial product from which NO_2 was removed by passage through a silica gel trap at –78°(25).

All phosphines were commercial materials and were recrystallized or distilled under nitrogen before using. Tris(p-fluorophenyl)phosphine was made by the standard Jensen method(26) and 1,1,1-tris(diphenylphosphinomethyl)ethane by Siegl's method.(27)

Preparation of the complexes.

Method A[8a,b]

Nitrosyltris(triphenylphosphine)cobalt. 1.10 g (3.58 mmoles of $[Co(NO)_2Cl]_2$[28] and a six-fold excess of triphenylphosphine were mixed under argon in 40 ml THF over an excess of 1% Na/Hg amalgam. The mixture was stirred for two hours; then the solution was poured off the amalgam and filtered through a Schlenk fritte to give a deep violet solution. After

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(23) G. La Monica, G. Navazio, P. Sandrini, and S. Cenini *J. Organometal. Chem.*, *31*, 89 (1971).

(24) M. G. Hogben and W. A. Graham, *J. Am. Chem. Soc.*, *91*, 283 (1969).

(25) E. E. Hughes, *J. Chem. Phys.*, *35*, 1531 (1961).

(26) K. A. Jensen, *J. Prakt. Chem.*, *148*, 101 (1937).

(27) W. O. Siegl, S. I. Lapporte, and J. P. Collman, *Inorg. Chem.*, *10*, 2158 (1971).

(28) W. Hieber and R. Marin, *Z. Anorg. Allgem. Chem.*, *240*, 241 (1939).

concentration of the solution, a three-fold excess of MeOH was added and $CoNO(P(C_6H_5)_3)_3$ precipitated as violet crystals which were washed with MeOH and MeOH-Et_2O (νNO 1640 cm^{-1}). Yield 80%. $C_{54}H_{45}NOCoP_3$ requires C = 74.00; H = 5.15; N = 1.6; P = 10.60; found C = 73.15; H = 5.36; N = 1.39; P = 10.50.

Nitrosyltris(diphenylmethylphosphine)cobalt. The red-orange compound was prepared as above from $[Co(NO)_2Cl]_2$[28] (0.22 g, 0.715 mmole) and a six-fold excess of diphenylmethylphosphine. Yield 85% (νNO 1630 cm^{-1}). $C_{39}H_{39}NOCoP_3$ requires C = 68.01; H = 5.67; N = 2.03; P = 13.48; found C = 66.44; H = 5:66; N = 2.04; P = 13.62.

Nitrosyltris(triphenylphosphine)rhodium. The red compound was prepared and purified as above using $[Rh(NO)_2Cl]_2$ (300 mg, 0.76 mmole) with a six-fold excess of phosphine. Yield 75% (νNO 1612 cm^{-1}). $C_{54}H_{45}NORhP_3$ requires C = 70.9; H = 3.27; P = 10.1; N = 1.52; found C = 70.5; H = 3.25; P = 9.8; N = 1.50.

Nitrosyltris(diphenylmethylphosphine)rhodium. 0.328 g (0.85 mmole) of $[Rh(NO)_2Cl]_2$ and a six-fold excess of phosphine were stirred for two hours in 15 ml THF over excess 1% Na/Hg. After filtration the resulting red-orange solution was concentrated to an oil. This oil was dissolved in a minimal amount of EtOH and excess petroleum ether was added. From the cold solution $RhNO(P(C_6H_5)_2(CH_3))_3$ came out as red-orange crystals in 80% yield (νNO 1570 cm^{-1}). $C_{39}H_{39}NORhP_3$ requires C = 64.00; H = 5.32; N = 1.92; P = 12.6; found C = 64.31; H = 5.32; N = 1.78; P = 12.2.

Nitrosyltris(tri-p-tolylphosphine)rhodium. The general Method A was used to form the red compound from $[Rh(NO)_2Cl]_2$ and phosphine in 80% yield (νNO 1600 cm^{-1}). $C_{63}H_{63}NORhP_3$ requires C = 72.10; H = 6.01; N = 1.35; P = 8.90; found C = 71.90; H = 6.21; N = 1.29; P = 8.85.

Nitrosyltris(tri-p-fluorophenylphosphine)rhodium. The preparation was carried out using the general Method A with $[Rh(NO)_2Cl]_2$ and a six-fold excess of $P(p\text{-}FC_6H_4)_3$ over 1% Na/Hg. The red compound was precipitated by addition of MeOH (νNO 1630 cm^{-1}). $C_{54}H_{36}F_9NORhP_3$ requires C = 59.65; H = 3.40; N = 1.29; P = 8.55; F = 16.00; found C = 59.65; H = 3.35; N = 1.25; P = 8.60; F = 16.00.

Method B.

Nitrosyltris(triphenylphosphine)rhodium. In a three-neck flask with NO and N_2 inlets a solution of 0.670 g (0.724 mmole) $RhCl(P(C_6H_5)_3)_3$ in 70 ml benzene was prepared under argon. The red solution turned pale green on addition of NO with rapid stirring.[8d] After one hour the NO flow was stopped and excess NO was purged with N_2. The green solution was then poured over excess 1% Na/Hg in 80 ml THF containing 1.2 g triphenylphosphine ($P(C_6H_5)_3$:Rh = 6). The reaction vessel was closed and the mixture was stirred overnight at room temperature; the solution turned from green to red. Next the solution was decanted from the amalgam and filtered in Schlenk apparatus. Concentration of the solution followed by addition of MeOH precipitated 300 mg $RhNO(P(C_6H_5)_3)_3$ (νNO 1612 cm^{-1}).

Method C.

Nitrosyltris(triphenylphosphine)rhodium. In a 500 ml three-neck flask with NO- and N_2- inlets and condenser, hydrated rhodium trichloride (2.0 g, 7.55 mmoles), triphenylphosphine (15.5 g, 59.5 mmoles) and granular zinc (13.8 g; Zn:Rh = 50) were mixed in 250 ml THF. The granular zinc had been previously activated by dilute hydrogen chloride, then washed with degassed water and THF and dried under vacuum. The mixture was stirred and heated to reflux while the NO was bubbled through, moderately fast for the first half hour and then more slowly for 10 hours. The NO flow was stopped, and the mixture was flushed with nitrogen, cooled, and filtered in a Schlenk tube to give a dark red solution. The filtrate was concentrated to 80 ml and then 800 ml MeOH was added to precipitate the red crystals of $RhNO(P(C_6H_5)_3)_3$ (6.0 g, 6.55 mmole, yield 80%) which were washed with MeOH and MeOH-Et_2O and dried *in vacuo*.

Nitrosyltris(triphenylphosphine)iridium. The same procedure as above was used with hydrated iridium trichloride (0.50 g, 1.39 mmoles), triphenylphosphine (4.0 g, 15.2 mmoles), and granular zinc (4.5 g; Zn: Ir = 50) in 150 ml THF. 550 mg yellow $IrNO(P(C_6H_5)_3)_3$ was obtained (0.55 mmoles, 40%), (νNO 1600 cm^{-1}). $C_{54}H_{45}IrNOP_3$ requires C = 64.25; H = 4.5; N = 1.4; P = 9.3; found C = 64.4; H = 4.55; N = 1.3; P = 9.05.

Method D.

Nitrosyltris(triphenylphosphine)rhodium. A two-step modification of the method of Levison and Robinson[8c] was used. A refluxing solution of triphenylphosphine (3.7 g, 14 mmole) in EtOH (150 ml) under argon was treated successively (rapid dropwise addition) with $RhCl_3{\cdot}3H_2O$ (0.50 g, 2.1 mmole) in EtOH (40 ml) and $NaBH_4$ (1.0 g, 26 mmole) in EtOH (50 ml); brown crystals were observed shortly in the reaction mixture. After 1/2 hour of refluxing, the mixture was cooled and filtered in Schlenk apparatus. The brown solid, $RhH(P(C_6H_5)_3)_4$, was washed through the fritte with a solution of N-methyl, N-nitroso-*p*-toluenesulfonamide (Diazald, 0.50 g, 2.4 mmole) in THF (150 ml) giving a dark red-brown solution. The mixture was stirred three hours. Then an equal volume of EtOH was added and the solution was concentrated until dark red crystals formed. These were filtrered in a Schlenk fritte and washed with 2:1 EtOH:Et_2O and EtOH. Yield 1.32g (72%).

Method E.

Nitrosyltris(triphenylphosphine)iridium. A) 365 mg (0.765 mmole) $Ir(P(C_6H_5)_3)_2N_2Cl$[29] was put in a 100 ml three-neck flask fitted with stirring bar, N_2-and NO-inlets. With N_2 flowing the NO flow was started.

55 ml of benzene was added to the purged vessel to give a red solution. In 15 minutes all the solid was in solution. After 3-1/2 hours of moderate NO bubbling, the NO flow was stopped and the solution purged with nitrogen.

B) An amalgam of Na/Hg (0.250 g. Na and 4 ml Hg) was prepared under N_2 in a 250 ml round bottom flask with gas inlets. 75 ml THF and 1.23 g triphenylphosphine were added. The red solution (part A) was poured in and the mixture stirred overtinght. The solution changed shortly to yellow-orange. The solution was decanted from the amalgam, concentrated, and treated with excess MeOH to precipitate the crude product.

Rechrystallization from THF/methanol gave pure crystals of the yellow $IrNO(P(C_6H_5)_3)_3$ (350 mg, 0.35 mmole, 45.5%).

Preparation of $[Rh(NO)_2Cl]_2$. 2.6g $[Rh(CO)_2Cl]_2$[30] was dissolved in 275 ml CCl_4 in a three-neck flask fitted with NO- and N_2- inlets. NO was bubbled in after purging with N_2. After 6 hours a dark brown solid precipitated. The bubbling was stopped and 2.6 g $[Rh(NO)_2Cl]_2$ was filtered out. RhN_2O_2Cl requires N = 14.20; Cl = 18.1; found N = 14.10; Cl = 18.3.

Preparation of nitrosyl-1,1,1-tris(diphenylphosphinomethyl)ethanerhodium. 0.735 g (0.80 mmole) $RhNO(P(C_6H_5)_3)_3$ was dissolved in 30 ml THF and 0.500 g (0.80 mmole) 1,1,1-tris(diphenylphosphinomethyl)ethane was added in 5 ml THF. The solution was stirred 12 hours at room temperature with a color change from red to yellow-orange. Then the solution was concentrated, and $RhNO[CH_3\text{-}C(CH_2P(C_6H_5)_2)_3]$ crystallized on addition of excess EtOH (νNO 1590 cm^{-1}). $C_{41}H_{39}$ $NORhP_3$ requires C = 65.03; H = 5.2; N = 1.85; P = 12.3; found C = 64.5; H = 5.33; N = 1.78; P = 12.1.

Addition of carbon monoxide.

Nitrosylcarbonylbis(triphenylphosphine)rhodium. A solution of 0.10g (0.11 mmole) $RhNO(P(C_6H_5)_3)_3$ in 10 ml benzene was stirred under 60 psig CO for 2 days at 25° with no color change. After CO was vented, 25 ml MeOH was added and the solution allowed to sit at 5°C for several days during which red crystals of $Rh(NO)(CO)(P(C_6H_5)_3)_2$ formed. These were filtered and washed with MeOH (νNO 1670 cm^{-1}, νCO 1970 cm^{-1}). $C_{37}H_{30}NO_2RhP_2$ requires C = 56.6; H = 3.87; N = 1.75; P = 7.92; found C = 57.1; H = 3.90; N = 1.70; P = 7.80.

Nitrosylcarbonylbis(triphenylphosphine)cobalt. The reaction was carried out as above with 0.200 g (0.229 mmole) $CoNO((P(C_6H_5)_3)_3$ for 24 hours in 20 ml benzene. Addition of MeOH precipitated $Co(NO)(CO)(P(C_6H_5)_3)_2$ as red-brown crystals (νNO 1717 cm^{-1}, νCO 1932 cm^{-1}). $C_{37}H_{30}NO_2CoP_2$ requires C = 69.3; H = 4.67; N = 2.18; P = 9.60; found C = 69.1; H = 4.55; N = 2.10; P = 9.50.

Reactions with hydrogen chloride.

Stoichiometric amount.

Addition to nitrosylstris(triphenylphosphine)rhodium. To a benzene solution (30 ml) of $RhNO(P(C_6H_5)_3)_3$ (300 mg, 0.327 mmole) was added a stoichiometric amount of HCl (using a benzene solution of known concentration). The solution lightened from red-orange and $RhCl_2NO(P(C_5H_6)_3)_2$ precipitated as orange crystals (197 mg, 45%) . The same reaction occurs with HCl gas but it was difficult to add stoichiometric amounts (νNO 1630 cm^{-1}). $C_{36}H_{30}Cl_2RhNOP_2$ requires C = 59.6; H = 4.12; N = 1.94; P = 8.55; Cl = 9.8; found C = 59.46; H = 4.30; N = 1.73; P = 8.8; Cl = 9.21.

Addition to nitrosyltris(triphenylphosphine)cobalt. To a benzene solution (20 ml) of $CoNO(P(C_6H_5)_3)_3$ (200 mg, 0.23 mmole) a stoichiometric amount of HCl (using a benzene solution of known concentration) was added. The solution changed from violet to brown. On addition of MeOH and concentration of the solution, the dark brown $CoCl_2NO(P(C_6H_5)_3)_2$ crystallized out (150 mg, 0.212 mmoles) (νNO 1640 cm^{-1}(s), 1760 cm^{-1} (w)). $C_{36}H_{30}Cl_2CoNOP_2$ requires C = 65.00; H = 4.44; N = 2.18; P = 9.20; Cl = 11.00; found C = 63.90; H = 4.50; N = 2.09; P = 9.40; Cl = 11.20.

Excess HCl.

Addition to nitrosyltris(triphenylphosphine)rhodium. An excess of anhydrous HCl gas was bubbled through a dichloromethane solution (30 ml) of $RhNO(P(C_6H_5)_3)_3$ (300 mg, 0.327 mmole). The solvent was removed under reduced pressure giving an orange solid, which was passed down a silica gel column (elution with dichloromethane). The first orange fraction contained $RhCl_2NO(P(C_6H_5)_3)_2$ and the second yellow fraction $RhCl_3(NH_2OH)(P(C_6H_5)_3)_2$. The latter was crystallized by adding MeOH and concentrating the solution; its infrared spectrum shows bands due to the coordinated hydroxylamine (3280 cm^{-1} (w)), 3230 cm^{-1} (w), νRh-Cl 338, 318 cm^{-1}). $C_{36}H_{33}Cl_3RhNOP_2$ requires C = 56.4; H = 4.30; N = 1.82; P = 8.08; found C = 55.9; H = 4.30; N = 1.20; P = 7.29.

If the reaction is run with excess DCl, N-D bands are noted at 2460 and 2380 cm^{-1}.

Separation of supposed "trichloronitroxylbis(triphenylphosphine)rhodium" into dichloronitrosylbis(triphenylphosphine)rhodium and trichloro-hydroxylaminebis(triphenylphosphine)rhodium. A sample of "$RhCl_3(HNO)(P(C_6H_5)_3)_2$" was chromatographed on silica gel (Baker, 40-140 mesh). Elution with CH_2Cl_2 gave a rapidly-moving orange-brown band; removal of solvent gave a solid whose infrared was identical to that of a known sample of $RhCl_2NO(P(C_6H_5)_3)_2$. Elution with acetone produced a yellow band; removal of sol-

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vent gave a solid whose infrared was identical to that of $RhCl_3(NH_2OH)(P(C_6H_5)_3)_2$.

Addition to nitrosyltris(triphenylphosphine)cobalt. Excess anhydrous HCl was bubbled through a benzene solution (20 ml) of $CoNO(P(C_5H_5)_3)_3$ (200 mg, 0.23 mmole). The violet solution turned first brown, then green while the blue complex $CoCl_2(P(C_5H_5)_3)_2$ came out (120 mg, 0.181 mmole). $C_{36}H_{30}CoCl_2P_2$ requires C = 66.00; H = 4.66; Cl = 11..00; P = 9.45; found C = 66.00; H = 4.52; Cl = 11.05: P = 9.30.

Reaction with benzoyl chloride.

Addition to nitrosyltris(triphenylphosphine)rhodium. To a solution of $RhNO(P(C_6H_5)_3)_3$ (200 mg, 0.218 mmole) in benzene (20 ml), was added 0.22 mmole of freshly distilled benzoyl chloride. The mixture was stirred for two hours with a color change from dark red to pale olive-green. Addition of MeOH to the concentrated solution precipitated the green compound $RhCl(PhCO)(NO)(P(C_5H_5)_3)_2$ which was recrystallized from THF-MeOH (90 mg, 0.11 mmole, 53%). (νNO 1608 cm^{-1}, νCO 1660 cm^{-1}). $C_{22}H_{35}NO_2ClRhP_2$ requires C = 64.7; H = 4.42; N = 1.75; Cl = 4.44; P = 7.77; found C = 63.44; H = 4.55; N = 1.92; Cl = 4.54; P = 7.75.

Rearrangement of $Rh(NO)(P(C_6H_5)_3)_2(PhCO)Cl$. 117 mg $RhCl(PhCO)(NO)(P(C_6H_5)_3)_2$ was dissolved in 20 ml THF to give a clear olive-green solution. The solution was left in a sealed tube under argon for 7 days while the color changed to brown. Then it was filtered in a Schlenk tube; 40 ml MeOH was added slowly, and a brown solid came out. This compound was characterized by infrared and elemental analysis as $RhCl(Ph)(NO)(CO)(P(C_6H_5)_3$ (νCO 1970 cm^{-1}, νNO 1630 cm^{-1}) $C_{25}H_{20}NO_2ClRhP$ requires C = 56.1; H = 3.75; Cl = 6.62; N = 2.61; P = 5.78; found C = 55.9; H = 3.80; Cl = 6.50; N = 2.52; P = 5.70.

Heating the green solution produced $Rh(Cl)(CO)(P(C_6H_5)_3)_2$ quantitatively (νCO 1960 cm^{-1}).

Reaction with benzoyl chloride under reflux. 407 mg (0.422 mmole) $RhNO(P(C_6H_5)_3)_3$ was stirred with 0.450 mmole benzoyl chloride in refluxing THF under nitrogen for eight hours to give a yellow-brown solution. After concentration and addition of MeOH to the solution, a yellow solid formed. Recrystallization from $CHCl_3$/MeOH yielded 250 mg $Rh(CO)(Cl)(P(C_5H_5)_3)_2$.

Addition to nitrosyltris(triphenylphosphine)cobalt. To a solution of $CoNO(P(C_6H_5)_3)_3$ (200 mg, 0.23 mmole) in 20 ml THF was added 0.239 mmole freshly distilled C_6H_5COCl. The solution was stirred under argon for two hours at 25°. $Co(NO(CO)(P(C_5H_5)_3)_2$ was precipitated as brown crystals by addition of MeOH (νNO 1714 cm^{-1}, νCO 1932 cm^{-1}). $C_{37}H_{30}CoNO_2P_2$ requires C = 69.3; H = 4.67; N = 2.18; P = 9.60; found C = 69.1; H = 4.55; N = 2.10; P = 9.50.

Chlorobenzene was detected in the solution by G.L.C. (a silicone column at 110°).

Reactions with p-toluenesulfonyl chloride. A benzene solution (5 ml) of 42.5 mg p-toluenesulfonyl chloride (0.220 mmole) was added to a solution of 200 mg (0.217 mmole) $RhNO(P(C_5H_5)_3)_3$ in 25 ml benzene and the mixture was stirred for several hours. As the reaction proceded, the orange $RhCl_2NO(P(C_6H_5)_3)_2$ crystallized from the solution; the reaction was completed overnight. Yield 74.0 mg, 44.5% (νNO 1630 cm^{-1}). $C_{36}H_{30}RhNOCl_2P_2$ requires C = 59.6; H = 4.12; N = 1.94; Cl = 9.21; P = 8.8; found C = 59.4; H = 4.30; N = 1.73; P = 8.8; Cl = 9.21.

Any sulfur dioxide formed was flushed from the reaction mixiture by N_2 bubbling and trapped in a water-methanol solution of known iodine concentration. Titration of this solution with a standard $Na_2S_2O_3$ solution showed that no iodine was consumed.

The presence of di(p-tolyl)disulfone in solution was confirmed by T.L.C. by comparison with a sample prepared independently.

Reaction with nitrosyltris(tri-p-tolylphosphine)rhodium. Reaction of equimolar quantities of $RhNO(P(p\text{-}CH_3C_6H_4)_3)_3$ and p-toluenesulfonyl chloride in benzene formed the dichloro complex $RhCl_2NO(P(p\text{-}CH_3C_6H_4)_3)_2$ in 46% yield. The disulfone was detected by T.L.C. $C_{38}H_{42}Cl_2RhNOP_2$ requires C = 59.5; H = 5.2; P = 7.30; N = 1.84; found C = 59.4; H = 5.1; P = 7.2; Cl = 8.5; N = 1.79; νNO 1620 cm^{-1}.

Reaction with nitrosyltris(triphenylphosphine) iridium. The reaction between $IrNO(P(C_6H_5)_3)_3$ (300 mg, 0.3 mmole) and a stoichiometric amount of *p*-toluenesulfonyl chloride (0.3 mmole) in benzene (30 ml) formed $IrCl_2NO(P(C_6H_5)_3)_2$ (115 mg, 0.141 mmole: 47%); di(p-tolyl)disulfone was detected by T.L.C. $C_{36}H_{30}Cl_2IrNOP_2$ requires C = 52.9; H = 3.7; N = 1.7; P = 7.56; Cl = 8.70; found C = 52.4; H = 3.92; N = 1.6; P = 7.56; Cl = 8.70.

Preparation of $MNO(P(C_6H_5)_3)_2I_2$ (M = Co, Rh) with HgI_2. Diiodonitrosylbis(triphenylphosphine) rhodium. A solution of 350 mg $RhNO(P(C_6H_5)_3)_3$ (0.38 mmole) and 180 mg HgI_2 (0.400 mmole) in 50 ml THF was stirred 3 hours. The solution was then filtered; the filtrate was concentrated and treated with excess MeOH to give microcrystals of $RhI_2NO(P(C_6H_5)_3)_2$ which were washed with ether and dried *in vacuo*. Yield 325 mg (0.356 mmole, 87.5%). $C_{36}H_{30}NORhI_2$ requires C = 47.4; H = 3.32; N = 1.54; P = 6.80; I = 27.9; found C = 47.83; H = 3.40; N = 1.57; P = 6.70; I = 27.2.

Diiodonitrosylbis(triphenylphosphine)cobalt. The preparation was carried out as above with 200 mg $Co(NO)(P(C_6H_5)_3)_3$ (0.23 mmole) in THF with a stoichiometric amount of HgI_2. Yield 30%. $C_{36}H_{30}NOCoI_2P_2$ requires C = 48.2; H = 3.36; N = 1.56; P = 6.92; I = 28.2; found C = 47.3; H = 3.34; N = 1.52; P = 6.29; I = 27.9.

with I_2

Diiodonitrosylbis(triphenylphosphine)rhodium. 150 mg $RhNO(P(C_5H_5)_3)_3$ (0.163 mmole) in 20 ml THF was treated with a stoichiometric amount of iodine.

The solution was stirred for three hours, filtered, and concentrated. Addition of 50 ml MeOH gave dark red microcrystals of $RhI_2NO(P(C_6H_5)_3)_2$ (120 mg, 0.121 mmole).

Diiodonitrosylbis(triphenylphosphine)cobalt. The reaction was carried out as above with 500 mg $CoNO(P(C_6H_5)_3)_3$ (0.572 mmole) in 20 ml THF and a stoichiometric amount of iodine. 300 mg $CoI_2NO(P(C_6H_5)_3)_2$ was obtained (0.335 mmole).

Disproportionation of diiodonitrosybis(triphenyl phosphine) cobalt. 200 mg (0.224 mmole) $CoI_2NO(P(C_6H_5)_3)_2$ was dissolved in 20 ml THF and excess MeOH was added to precipitate the compound. Cooling the solution in a freezer for three days produced deep-brown crystals of $Co(NO)_2(P(C_6H_5)_3)I$, which were filtered, washed with MeOH, and dried *in vacuo* (40 mg, 0.0985 mmole). $C_{18}H_{15}N_2O_2CoIP$ requires C = 43.10; H = 3.01; N = 5.6; P = 6.2; I = 25.5; found C = 42.42; H = 2.86; N = 4.91; P = 6.03; I = 24.86.

The filtrate was concentrated and treated with benzene. Green crystals of $Co(P(C_6H_5)_3)_2I_2$ formed. $C_{36}H_{30}CoI_2P_2$ requires C = 51.6; H = 3.58; P = 7.41; I = 30.4; found C = 50.8; H = 3.70; P = 7.30; I = 30.7.

Reactions of dihalonitrosyls with CO. A solution of 0.24 g (0.40 mmole) $RhCl_2NO(P(CH_3)(C_6H_5)_2)_2$ in 10 ml CH_2Cl_2 (some air present) was stirred under 1 atm CO in a flask fitted with rubber septum. Liquid samples were withdrawn for infrared analysis by syringe. Similar reactions were run with $RhI_2NO(P(C_6H_5)_3)_2$ and $IrI_2NO(P(C_6H_5)_3)_2$.

Dinitrosylbis(triphenylphosphine)iridium hexafluorophosphate. 300 mg $IrNO(P(C_6H_5)_3)_3$ (0.30 mmoles) in 35 ml dry degassed benzene was treated with 63 mg (0.33 mmole) $NOPF_6$ in 2 ml MeOH under argon. The solution turned from orange to deep red. After several hours, deep red crystals of $[Ir(NO)_2(P(C_6H_5)_3)_2]^+ PF_6^-$ formed. The solid was filtered, washed with benzene containing a little MeOH, and dried *in vacuo* (200 mg, 0.216 mmole). $C_{36}H_{30}N_2O_2IrP_3F_6$ requires C = 46.8; H = 3.26; P = 10.1; N = 3.05; found C = 47.9; H = 3.48; P = 9.05; N = 3.00.

$[Ir(NO)_2(P(C_6H_5)_3)_2]PF_6$ in 85% yield was also obtained by the reaction of $Ir(CO)(NO)(P(_6H_5)_3)_2$ 235 mg, 0.303 mmole) in 20 ml benzene with 60 mg (0.31 mmole) $NOPF_6$ in 2 ml MeOH. The compound was filtered, washed with benzene/MeOH, and dried *in vacuo* (240 mg, 0.260 mmole).

Dinitrosylbis(triphenylphosphine)rhodium hexafluorophosphate. The reaction was carried out as above with 300 mg (0.325 mmole) $RhNO(P(C_6H_5)_3)_3$ in 35 ml benzene and 72 mg (0.325 mmole) $NOPF_6$ in 2 ml MeOH. 220 mg (0.257 mmole $[Rh(NO)_2(P(C_6H_5)_3)_2]^+PF_6^-$, was collected as deep brown crystals on filtration and washing with benzene/MeOH. $C_{36}H_{30}N_2O_2RhP_3F_6$ requires C = 53.00; H = 3.61; N = 3.36; P = 11.20; found C = 51.61; H = 3.64; N = 3.42; P = 10.86.

Reaction of $IrI_2NO(P(C_6H_5)_3)_2$ with $NOPF_6$. 56.16 mg (0.0500 mmole) $IrI_2NO(P(C_6H_5)_3)_2$ in 10 ml benzene was treated with 12 mg (0.050 mmole) $NOPF_6$ in 1 ml methanol. No change was detected in the orange solution. 52 mg starting material was recovered upon concentration of the solution.

Reaction of $RhI_2NO(P(C_6H_5)_3)_2$ with $NOPF_6$. $RhI_2NO(P(C_6H_5)_3)_2$ (50.65 mg, 0.0505 mmole) in 10 ml benzene was treated with 12 mg (0.050 mmole) $NOPF_6$. No change was detected in the solution; 48 mg starting material was recovered on concentration of the solution.

Isomerization of 1-hexene by $Rh(NO)(P(C_6H_5)_3)_3$ in CH_2Cl_2. A solution of $Rh(NO)(P(C_6H_5)_3)_3$ (38 mg, 0.041 mmole) and 1-hexene (0.3 ml, 2 mmole) in CH_2Cl_2 (6 ml) was was stirred under argon for two days. G.L.C. analysis of the solution showed no internal olefins present; the red color of the solution had not changed. A brief exposure of the solution to air resulted in 10% conversion to internal olefins in five hours.

Formation of $Rh(NO)(P(C_6H_5)_3)_3$ by reduction of $RhCl_2NO(P(C_6H_5)_3)_2$ with sodium amalgam in the presence of excess $P(C_6H_5)_3$. A slurry of $RhCl_2NO(P(C_6H_5)_3)_2$ (90 mg, 0.12 mmole) and $P(_6H_5)_3$ (90 mg, 0.38 mmole) in 12 ml THF was stirred over a twentyfold excess of 1% Na/Hg for sixteen hours. Then the supernatant solution was drawn off and transferred by needle stock to a Schlenk apparatus in which it was filtered through Florisil. The blood-red filtrate was concentrated and treated with excess MeOH to precipitate red microcrystals which were filtered and washed thoroughly with MeOH. Yield 82 mg (72%). $Ir(NO)(P(C_6H_5)_3)_3$ was prepared similarly from $IrCl_2NO(P(C_6H_5)_3)_2$ and $IrI_2NO(P(C_6H_5)_3)_2$ in 82% and 84% yields respectively.

Attempted Syntheses of $M(NO)(P(C_6H_5)_3)_2Z$ by reduction of $MX_2NO(P(C_6H_5)_3)_2$ with sodium amalgam in the presence of excess Z (M = Rh, Ir). Reactions were carried out as above with $RhCl_2NO(P(C_6H_5)_3)_2$ and $IrI_2NO(P(C_6H_5)_3)_2$ using Z = C_2H_4, $C_6H_5C{\equiv}CC_6H_5$, CH_3CN, C_5H_5N ($Z{:}M \simeq 50$) in place of $P(C_6H_5)_3$. For all Z only $Rh(NO)(P(C_6H_5)_3)_3$ in moderate yields (40-50%) could be isolated.

Synthesis of $Rh(NO)(P(C_6H_5)_3)_3$ by reduction of $RhCl_2NO(P(C_6H_5)_3)_2$ with H_2 and K_2CO_3 in the presence of excess $P(C_6H_5)_3$. A slurry of $RhCl_2NO(P(C_6H_5)_3)_2$· (102 mg, 0.14 mmole), $P(C_6H_5)_3$ (61 mg, 0.23 mmole). and anhydrous K_2CO_3 (0.73 g, 5.2 mmole) in 20 ml THF was stirred under 8 atm H_2 in a Fischer-Porter bottle for 15 hours at 25°, with no apparent reaction. Then the bottle was placed in an oil bath at 65° and the mixture stirred four hours; the dichloronitrosyl dissolved fairly rapidly with formation of a blood-red solution. The solution was cooled and filtered. The filtrate was concentrated and treated with excess MeOH, forming red microcrystals which were filtered and washed with MeOH. Yield 76 mg (59%). The analagous reduction of $IrI_2NO(P(C_6H_5)_3)_2$ did not occur at 8 atm H_2 until the temperature was raised to 90°; heating the slurry four hours slowly produced a pale yellow solution.

This solution was worked up as above to give primarily light yellow crystals with ν N-O at 1750 cm^{-1} with a small amount of orange crystals (Ir(NO)-$(P(C_6H_5)_3)_3$).

Attempted synthesis of Rh(NO)$(P(C_6H_5)_3)_2$Z by reduction of $RhCl_2NO(P(C_6H_5)_3)_2$ with H_2 and K_2CO_3 followed by addition of excess Z. The reductions were carried out as above except with $P(C_6H_5)_3$ absent. The resulting solutions (identical in color to those above for $RhCl_2NO(P(C_6H_5)_3)_2$ + $P(C_6H_5)_3$ + H_2 + K_2CO_3 were treated with excess Z (Z = C_2H_4, $C_6H_5C{\equiv}CC_6H_5$, C_5H_5N, dimethyl maleate); no color change resulted. The solutions were filtered, concentrated, and treated with excess MeOH forming Rh(NO))$P(C_6H_5)_3)_3$ in moderate yields (40-50%) for all Z.

Catalytic hydrogenation with reaction mixtures of reduced $MCl_2NO(P(C_6H_5)_3)_3$ (M = Rh, Ir). The dichloronitrosyls were reduced by Na/Hg (M = Rh, Ir) or H_2 + K_2CO_3 (M = Rh) as previously described but in the absence of $P(C_6H_5)_3$ and any Z. The resulting reaction mixtures were put under 1 atm H_2 and 1.0 ml 1-hexene was aded. Then the pressure was increased to 2 atm H_2 and samples were withdrawn for G.L.C. analysis (2,4-dimethylsulfolane).

Catalytic Hydrogenation with M(NO)$(P(C_6H_5)_3)_2$ (maleic anhydride) (M = Rh, Ir). A solution of Rh(NO)-$(P(C_6H_5)_3)_2$ (maleic anhydride)[23] (43 mg, .057 mmole) in 10 ml CH_2Cl_2 was stirred under 4 atm H_2 for five hours at 25°. Then 1.0 ml 1-decene was injected and the solution stirred under 2 atm H_2. Samples were withdrawn for G.L.C. analysis (Carbowax 20 M). A similar reaction was carried out with the iridium analogue[23] (51 mg, .060 mmole) in CH_2Cl_2.

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