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REACTIONS OF NITROSONIUM ION WITH ANIONIC CARBONYL MONOMERS AND CLUSTERS. CRYSTAL AND MOLECULAR STRUCTURE OF $FeCo_2(\mu_3\text{-}NH)(CO)_9$

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Summary

The reactions of several mono- and poly-nuclear carbonyl metallates with nitrosonium ion have been studied. Besides simple substitution of a carbon monoxide with NO^+ some reactions yielded products containing other nitrogenous ligands. When $[CoRu_3(CO)_{13}]^-$ reacts with NO^+, low yields of the new nitrido cluster $CoRu_3N(CO)_{12}$ are formed. Prior conversion of $[CoRu_3(CO)_{13}]^-$ to the new hydrido cluster $[H_2CoRu_3(CO)_{12}]^-$ under hydrogen, followed by nitrosylation, forms the new imido cluster $H_2Ru_3(NH)(CO)_9$ in very low yield. The reaction of $[FeCo_3(CO)_{12}]^-$ with NO^+ also generates an imido cluster, $FeCo_2(NH)(CO)_9$, in 15% yield. This cluster has been characterized by X-ray crystallography and was found to be similar to the tricobalt alkylidyne clusters. (Triclinic crystal system, $P\bar{1}$ space group, $Z = 2$, a 6.787(1), b 8.016(1), c 13.881(2) Å, α 95.50(1), β 100.77(1), γ 107.93(1)°). Modifications of the nitrosylations using NO^+ were studied. In particular, the addition of triethylamine or *N*-t-butylbenzaldimine allowed the use of NO^+ in THF without solvent decomposition. With $[CpMo(CO)_3]^-$ and $[CpFe(CO)_2]^-$ the *N*-nitrosoiminium species appears to form transient alkylmetals which further react to give the dimers $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$.

Despite being one of the most useful nitrosylating reagents available, the reactivity of NO^+ with metal carbonyls is difficult to control [1]. Further, its ability to react with common solvents like alcohols and especially THF place additional limitations on its use. The desired product in most cases is the simple substitution of NO^+ for another two-electron donor, but this is often complicated by oxidation of the metal without formation of a coordinated nitrosyl. We present here a summary of reactions of mono- and poly-nuclear carbonyl anions with NO^+ under several different conditions. Several new species containing nitrogenous ligands, but not NO, are reported along with attempts to modify the reactivity of NO^+ with selected nitrogen donors.

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Experimental

Diethyl ether and tetrahydrofuran (THF) were freshly distilled over sodium benzophenone ketyl under nitrogen. Hexane was freshly distilled over phosphorus pentoxide under nitrogen, and acetonitrile was freshly distilled over calcium hydride under nitrogen. Triethylamine was stirred overnight over KOH and distilled under nitrogen. ^{1}H NMR spectra were obtained on a Varian Model CFT-20, and infrared spectra were obtained on a Beckman Model 4250. All reactions were carried out using standard Schlenk techniques, and transfers of air-sensitive materials were carried out in a Vacuum Atmospheres glove box. All chromatography was conducted on silica gel using hexane as the eluent.

$PPN[Fe(CO)_3(NO)]$ [2], $PPN[Mn(CO)_2(NO)_2]$ [2], $PPN[Fe_4N(CO)_{12}]$ [3], $PPN[Co(CO)_4]$ [4], $K[CpFe(CO)_2]$ [5], $K[CpMo(CO)_3]$ [5], $PPN[Mn(CO)_5]$ [6], $PPN[CoRu_3(CO)_{13}]$ [7], PPNCl [8], $PPN[Fe_3Co(CO)_{13}]$ [7], $Et_4N[FeCo_3(CO)_{12}]$ [9], $PPN_2[Fe_4(CO)_{13}]$ [10], $PPN[HFe_3(CO)_{11}]$ [11], and $PPN[HFe_4(CO)_{13}]$ [12] were prepared by standard literature techniques. *N*-t-butylbenzaldimine was prepared by a modification of literature methods [13]. $NOPF_6$ (Alfa-Ventron) was used as received.

$[PPN]_2[Fe_4(CO)_{13}] + NOPF_6$. $[PPN]_2[Fe_4(CO)_{13}]$ (450 mg, 0.270 mmol) and $NOPF_6$ (50 mg, 0.29 mmol) were placed in a Schlenk tube and 30 ml CH_2Cl_2 was added by syringe. After stirring for 1 h, the CH_2Cl_2 was removed under vacuum. The product was extracted into 50 ml Et_2O, filtered, and the Et_2O was removed on a rotary evaporator. The resultant oil was triturated with 2 ml EtOH to give 43 mg of black, crystalline $PPN[Fe_4N(CO)_{12}]$ (14%).

$PPN[Fe_3Co(CO)_{13}] + NOPF_6$. $PPN[Fe_3Co(CO)_{13}]$ (67 mg, 0.059 mmol) and $NOPF_6$ (13 mg, 0.074 mmol) were placed in a Schlenk tube and 25 ml CH_2Cl_2 was added by syringe. After stirring for 1 h, the CH_2Cl_2 was removed and the products were extracted into hexane. Chromatography gave three bands. The first was brown and contained $Fe_4N(CO)_{11}(NO)$, identified by its infrared spectrum. The second was green and contained $Fe_3(CO)_{12}$. The last band was brown and gave 6 mg of $FeCo_2(NH)(CO)_9$. Mass spectrum, 441 (P^+) followed by successive loss of 9 CO. Anal. Found: C, 24.41; H, 0.28; N, 3.15. $FeCo_2(NH)(CO)_9$ calcd.: C, 24.52; H, 0.23; N, 3.18%.

$Et_4N[FeCo_3(CO)_{12}] + NOPF_6$. $Et_4N[FeCo_3(CO)_{12}]$ (1.498 g, 2.143 mmol) and $NOPF_6$ (470 mg, 2.68 mmol) were placed in a Schlenk flask and 50 ml CH_2Cl_2 was added by syringe. After stirring vigorously for 2 h, the solvent was evaporated. The products were extracted into 4 × 50 ml Et_2O, followed by addition of 100 ml hexane to the extract which was then filtered. After allowing the filtrate to stand in air for 24 h to selectively decompose $Co_4(CO)_{12}$, it was again filtered to give a pure solution of $FeCo_2(NH)(CO)_9$. The solvent was removed and the residue washed with hexane to give 129 mg of black crystals (14%).

$PPN[CoRu_3(CO)_{13}] + NOPF_6$. $NOPF_6$ (25 mg, 0.14 mmol) and 10 ml CH_2Cl_2 were placed in a Schlenk tube and brought to reflux. $PPN[CoRu_3(CO)_{13}]$ (122 mg, 0.0965 mmol) was placed in another Schlenk tube and dissolved in 30 ml CH_2Cl_2. The cluster-containing solution was then added by cannula to the $NOPF_6$ and reflux was maintained for 1 h. After evaporating the solvent the product was extracted with hexane. Chromatography gave two products. The first band was yellow and contained $Ru_3(CO)_{12}$. The second band was orange and gave $CoRu_3N(CO)_{12}$ in 8%

yield (5.3 mg, 0.0074 mmol). Mass spectrum, 715–712 (P^+ envelope) followed by mass envelopes corresponding to loss of 12 CO, 322–313 (Ru_3N^+ envelope). Anal. Found: C, 20.13; N, 1.94. $CoRu_3N(CO)_{12}$ calcd.: C, 20.24; N, 1.97%.

Preparation of PPN[$H_2CoRu_3(CO)_{12}$]. A solution of PPN[$Co(CO)_4$] (567 mg, 0.801 mmol) and $Ru_3(CO)_{12}$ (499 mg, 0.781 mmol) in 150 ml THF was heated to reflux under a stream of N_2 (to remove CO) for 45 min. A solution infrared spectrum confirmed the formation of PPN[$CoRu_3(CO)_{13}$]. The N_2 stream was replaced with H_2 and the reflux was continued for 20 h. After removing the THF, the product was dissolved in 350 ml Et_2O and filtered. Addition of an equal volume of hexane to the ether solution gave red air-stable crystals. A second crop of crystals was collected by allowing the resulting ether/hexane solution to evaporate under reduced pressure. This gave 922 mg of PPN[$H_2CoRu_3(CO)_{12}$], 95% yield. Anal. Found: C, 46.40; H, 2.65. PPN[$H_2CoRu_3(CO)_{12}$] calcd.: C, 46.54; H, 2.60%.

PPN[$H_2CoRu_3(CO)_{13}$] + $NOPF_6$. PPN[$H_2CoRu_3(CO)_{12}$] (110 mg, 0.089 mmol) and $NOPF_6$ (20 mg, 0.114 mmol) were placed in a Schlenk tube and 20 ml CH_2Cl_2 was added by syringe. After stirring for 30 m, the solvent was evaporated. Extraction of the products into hexane, followed by chromatography gave six products in four bands. The first band to elute was yellow and contained $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. The second band was red and contained $HRu_3(CO)_{10}(NO)$. The third band was also red and contained $H_2Ru_4(CO)_{13}$ and $H_3CoRu_3(CO)_{12}$. The fourth band was yellow and gave $H_2Ru_3(NH)(CO)_9$ in 4% yield (2 mg, 0.035 mmol). Mass spectrum, 577–568 (P^+ envelope) followed by mass envelopes corresponding to loss of 9 CO and H_2. High resolution mass spectrum calculated for [$H_2{}^{102}Ru_3(NH)(CO)_9$]: 574.6938. Found: 574.6936.

Et_4N[$HFe_3(CO)_{11}$] + $NOPF_6$. $Et_4N[HFe_3(CO)_{11}]$ (507 mg, 0.836 mmol) and $NOPF_6$ (167 mg, 0.952 mmol) were placed in a Schlenk tube and 50 ml CH_2Cl_2 was added by syringe. After stirring for 30 min, the solvent was removed. $Fe(CO)_5$ and $Fe(CO)_2(NO)_2$ were removed with the solvent as the major products. Extraction of the solid residue with hexane gave a small amount of $Fe_3(CO)_{12}$. No other tractable products were identified.

PPN[$HFe_4(CO)_{13}$] + $NOPF_6$. PPN[$HFe_4(CO)_{13}$] (1.23 g, 1.10 mmol) and $NOPF_6$ (193 mg, 1.10 mmol) were placed in a flask and 90 ml CH_2Cl_2 was added by syringe. After stirring the solution for 1 h, the solvent was removed under vacuum. An infrared spectrum of the distillate verified the presence of $Fe(CO)_5$ and $Fe(CO)_2(NO)_2$. Extraction of the non-volatile residue with hexane gave $Fe_3(CO)_{12}$ as the only hexane soluble-product.

Reaction of PPN[$Fe(CO)_3(NO)$] with N-nitroso-N-t-butylbenzaldiminium hexafluorophosphate (NTBB). This procedure is representative of the reactions of the *N*-nitrosoiminium ion with the carbonylmetallates. A solution of benzaldehyde t-butylimine (25.4 mg, 0.158 mmol) in 2 ml THF was added dropwise to 27.6 mg $NOPF_6$. To this pale yellow homogeneous solution was added dropwise PPN[$Fe(CO)_3(NO)$] (56.0 mg, 0.079 mmol) in 3 ml THF. The solution was stirred at room temperature and the reaction monitored by IR. After 45 min the starting material had been consumed and the solution had turned red. The product $Fe(CO)_2(NO)_2$ and solvent were distilled into a flask cooled to − 196°C. Yield was 92% $Fe(CO)_2(NO)_2$ as determined by the intensity of the 2080 cm^{-1} stretch in the IR.

Reaction of [$Mo(\eta^5\text{-}C_5H_5)(CO)_3$]$^-$ with N-nitrosotriethylammonium hexafluoro-

phosphate. This procedure is representative of the reaction of the *N*-nitrosoammonium ion with the carbonylmetallates. Triethylamine (12.3 mg, 0.122 mmol) in 2 ml THF was added to $NOPF_6$ (21.3 mg, 0.122 mmol). A suspension of $K[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ (17.3 mg, 0.061 mmol) in 3 ml THF was added dropwise to the solution. The reaction was stirred at room temperature for one hour, after which time the solution was homogeneous. The solvent was evaporated and the residue sublimed (70°C, 0.3 torr) to yield 12 mg $CpMo(CO)_2(NO)$ (79%).

Collection and reduction of the X-ray data. A brown crystal of $FeCo_2(NH)(CO)_9$ was mounted on a glass fiber and found to be triclinic by the Enraf–Nonius CAD4-SDP peak search, centering, and indexing programs, and by a Delauney reduction calculation [14]. The centrosymmetric space group $P\bar{1}$ was chosen and data collection begun. Successful refinement of the structure verified the choice of this space group. A summary of the crystal data is presented in Table 1. The intensity data were measured with ω–2θ scans. Background counts of duration equal to one fourth of the scan time for each peak were measured at the two ends of the scan range. In this manner, the total duration of measuring background is equal to half of the time required for the peak scan. The three check reflections showed no change in intensity during data collection. The full sphere of data ($\pm h$, $\pm k$, $\pm l$) were collected out to 54° in 2θ, and the equivalent reflections were averaged. A total of 3040 unique reflections were measured, of which 2122 had $I > 3.0\sigma(I)$, and were used in the structural determination. The data were corrected for Lorentz, polarization, and background effects but not for absorption.

Solution and refinement of the structure. The structure was solved by conventional heavy-atom techniques. The positions of the three metal atoms were determined by a

TABLE 1

CRYSTAL PARAMETERS

crystal system, triclinic
space group, $P\bar{1}$
a 6.787(1) Å
b 8.016(1) Å
c 13.881(2) Å
α 95.50(1)°
β 100.77(1)°
γ 107.93(1)°

$V = 696.3(4)$ Å^3
$Z = 2$
calcd. density 2.10 g cm^{-3}
temp. 22°C
abs. coeff. 35.4 cm^{-1}
formula $C_9HCo_2FeNO_9$

MEASUREMENT INTENSITY DATA

diffractometer: Enraf–Nonius CAD4
radiation: Mo-K_α (λ 0.71069 Å)
monochromator: graphite crystal
scan speed: variable from 1.6 to 20 deg/min
scan range: $0° \leq 2\theta \leq 54°$
reflctns measd: $\pm h$ $\pm k$ $\pm l$
check reflection: (0, 4, 0), (0, 0, −10), (4, 0, 0); measured approximately every 200 reflections
reflections collected: 3040 unique; 2122 with $I > 3\sigma(I)$
$p = 0.05$
$R = 0.019$
$R_w = 0.027$

TABLE 2

BOND DISTANCES

Atoms	Distance (Å)	Atoms	Distance (Å)
M(1)–M(2)	2.479(1)	N–H	0.83(3)
M(1)–M(3)	2.476(1)	C(11)–O(11)	1.123(4)
M(2)–M(3)	2.489(1)	C(12)–O(12)	1.127(4)
M(1)–N	1.867(2)	C(13)–O(13)	1.131(4)
M(2)–N	1.850(2)	C(21)–O(21)	1.133(4)
M(3)–N	1.861(2)	C(22)–O(22)	1.129(3)
M(1)–C(11)	1.816(3)	C(23)–O(23)	1.129(4)
M(1)–C(12)	1.814(3)	C(31)–O(31)	1.130(4)
M(1)–C(13)	1.816(3)	C(32)–O(32)	1.133(4)
M(2)–C(21)	1.789(3)	C(33)–O(33)	1.133(3)
M(2)–C(22)	1.804(3)		
M(2)–C(23)	1.804(3)		
M(3)–C(31)	1.800(3)		
M(3)–C(32)	1.803(3)		
M(3)–C(33)	1.801(3)		

TABLE 3

SELECTED BOND ANGLES

Atoms	Angle (°)	Atoms	Angle (°)
M(1)–M(2)–M(3)	59.79(1)	C(11)–M(1)–M(2)	98.6(1)
M(2)–M(3)–M(1)	59.91(1)	C(11)–M(1)–M(3)	99.5(1)
M(3)–M(1)–M(2)	60.31(1)	C(11)–M(1)–N	139.9(1)
M(1)–N–M(2)	83.69(9)	C(12)–M(1)–M(2)	97.6(1)
M(2)–N–M(3)	84.26(9)	C(12)–M(1)–M(3)	151.8(1)
M(1)–N–M(3)	83.26(9)	C(12)–M(1)–N	104.4(1)
M(1)–N–H	136(2)	C(13)–M(1)–M(2)	152.0(1)
M(2)–N–H	126(2)	C(13)–M(1)–M(3)	97.3(1)
M(3)–N–H	126(2)	C(13)–M(1)–N	105.2(1)
M(1)–C(11)–O(11)	178.8(3)	C(21)–M(2)–M(1)	152.3(1)
M(1)–C(12)–O(12)	178.2(3)	C(21)–M(2)–M(3)	96.7(1)
M(1)–C(13)–O(13)	179.5(3)	C(21)–M(2)–N	105.7(1)
M(2)–C(21)–O(21)	179.7(3)	C(22)–M(2)–M(1)	100.6(1)
M(2)–C(22)–O(22)	179.0(3)	C(22)–M(2)–M(3)	102.8(1)
M(2)–C(23)–O(23)	178.8(3)	C(22)–M(2)–N	143.3(1)
M(3)–C(31)–O(31)	178.7(4)	C(23)–M(2)–M(1)	100.6(1)
M(3)–C(32)–O(32)	179.3(3)	C(23)–M(2)–M(3)	152.7(1)
M(3)–C(33)–O(33)	178.4(3)	C(23)–M(2)–N	105.0(1)
C(11)–M(1)–C(12)	101.1(1)	C(31)–M(3)–M(1)	152.4(1)
C(11)–M(1)–C(13)	101.8(1)	C(31)–M(3)–M(2)	98.6(1)
C(12)–M(1)–C(13)	97.1(1)	C(31)–M(3)–N	104.7(1)
C(21)–M(2)–C(22)	98.7(1)	C(32)–M(3)–M(1)	98.3(1)
C(21)–M(2)–C(23)	95.6(2)	C(32)–M(3)–M(2)	152.8(1)
C(22)–M(2)–C(23)	99.4(1)	C(32)–M(3)–N	106.2(1)
C(31)–M(3)–C(32)	95.7(2)	C(33)–M(3)–M(1)	100.3(1)
C(31)–M(3)–C(33)	100.2(2)	C(33)–M(3)–M(2)	99.2(1)
C(32)–M(3)–C(33)	100.9(1)	C(33)–M(3)–N	140.7(1)

Patterson synthesis. Subsequent structure factor and difference Fourier calculations revealed the positions of all remaining atoms [16]. All non-hydrogen atoms were refined with the use of anisotropic temperature factors, and the hydrogen atom was refined using isotropic temperature factors. The values of the atomic scattering factors used in the calculations were taken from the usual tabulation, and the effects of anomalous dispersion were included for the non-hydrogen atoms [17]. The hydrogen atom scattering factors were taken from Cromer and Ibers' list [18]. The metal atoms were refined as cobalt atoms, and in the last several cycles of least squares refinement the occupancy was allowed to vary, generating the values: 0.977 for M1, 0.967 for M2, and 0.979 for M3. The value of these numbers is questionable because of the strong coupling between the temperature factors and occupancies, and the small difference between the scattering factors for Fe and Co. Tables 2 and 3 contain the bond distance and angle data.

Results and discussion

Reactions of NO^+ with selected polynuclear metal carbonyl anions. Equations 1 through 7 summarize the reactions of NO^+ with several tri- and tetra-nuclear metal clusters. Except where specifically stated otherwise, all reactions were conducted at room temperature using a nearly stoichiometric amount of NO^+. With the exception of $[Fe_4(CO)_{13}]^{2-}$ (eq. 3) all clusters undergo extensive fragmentation generating low

$$[HFe_3(CO)_{11}]^- + NO^+ \rightarrow Fe(CO)_5 + Fe(CO)_2(NO)_2 + Fe_3(CO)_{12} \tag{1}$$

$$[HFe_4(CO)_{13}]^- + NO^+ \rightarrow Fe(CO)_5 + Fe(CO)_2(NO)_2 + Fe_3(CO)_{12} \tag{2}$$

$$[Fe_4(CO)_{13}]^{2-} + NO^+ \rightarrow [Fe_4N(CO)_{12}]^- \tag{3}$$

$$[Fe_3CO(CO)_{13}]^- + NO^+ \rightarrow$$
$$Fe(CO)_2(NO)_2 + Fe_4N(CO)_{11}(NO) + Fe_3(CO)_{12} + FeCo_2(NH)(CO)_9 \tag{4}$$

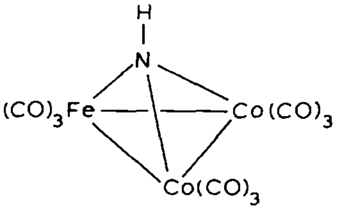
$$[FeCo_3(CO)_{12}]^- + NO^+ \rightarrow$$
$$Co(CO)_3(NO) + Fe(CO)_2(NO)_2 + Co_4(CO)_{12} + FeCo_2(NH)(CO)_9 \tag{5}$$

$$[CoRu_3(CO)_{13}]^- + NO^+ \rightarrow Co(CO)_3(NO) + Ru_3(CO)_{12} + CoRu_3N(CO)_{12} \tag{6}$$

$$[H_2CoRu_3(CO)_{12}]^- + NO^+ \rightarrow Co(CO)_3(NO) + Ru_3(CO)_{12} + H_2Ru_3(NH)(CO)_9 \tag{7}$$

yields of many products. In this regard there is a close similarity between the reactivity of NO^+ and CO, the latter also commonly leading to cluster fragmentation [19]. Several of the products were new and interestingly contain nitrogen in a reduced form such as NH or simply N.

$FeCo_2(NH)(CO)_9$. Reaction of either of the iron-cobalt cluster anions with $NOPF_6$ leads to the new imido cluster $FeCo_2(NH)(CO)_9$ in 10–15% yield. The spectroscopic properties of this and the other new clusters are listed in Table 4. The formulation is isoelectronic with the well known nonacarbonyl iron-dicobalt chalcogenide clusters [20] as well as the tricobalt (alkylidyne) species [24]. All of these have three terminal carbonyls bound to each metal, and a triply bridging CR or S ligand, suggesting structure I for $FeCo_2(NH)(CO)_9$.



(I)

Although clusters containing the μ_3-NH group have been observed [3], no structural analyses have been reported. Because of the possible analogy between a cluster-coordinated NH and NH coordinated to a metal surface, we conducted a single crystal X-ray crystallographic analysis of $FeCo_2(NH)(CO)_9$. Figure 1 is a view of the structure with the atomic labelling. The structure consists of three metal tricarbonyl groups in a triangular plane with a μ_3-NH symmetrically capping the plane, making the point group for the cluster C_{3v} disregarding the differences in the metals. It is noteworthy that the distances and angles suggest that a plane of symmetry passes through Ml. This implies that the Fe is preferentially located at M1 and Co at M2,3 or that Co is at M1 and Fe and Co are disordered at M2,3. Despite this we do not feel that we can confidently distinguish between the iron and the cobalt sites in the cluster as was also the case with earlier work with $FeCo_2S(CO)_9$ and its Se and Te analogs [20]. The M–M bond distances are slightly shortened relative to these $FeCo_2$(Chalcogenide)$(CO)_9$ clusters and are in line with species where the capping group is a first row element, such as carbon, in the $Co_3(CR)(CO)_9$ compounds [21]. No unusual features are associated with the μ_3-NH ligand. The N–H bond distance is 0.83(3) Å, which is quite similar to the N–H in $Mo_2O_3(\mu_2\text{-}NH)[S_2P(OC_2H_5)_2]_2 \cdot C_4H_8O$ [22].

$CoRu_3N(CO)_{12}$. The anionic cluster $[CoRu_3(CO)_{13}]^-$ is formed quantitatively by

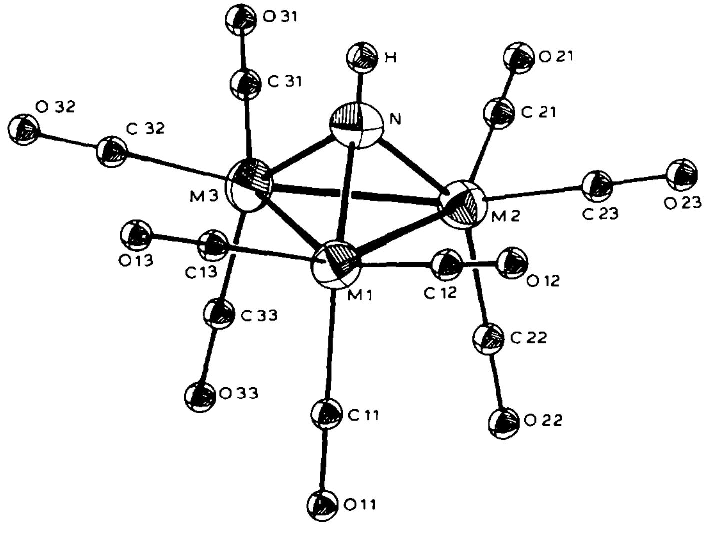


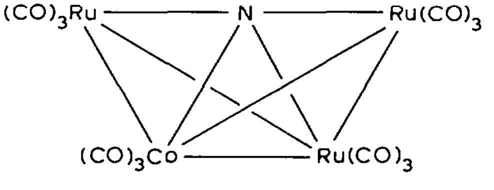
Fig. 1. View of $FeCo_2(\mu_3\text{-}NH)(CO)_9$ with atom labelling scheme.

TABLE 4

Cluster	Color	δ($CDCl_3$) (ppm)	ν(NH) (cm^{-1})	ν(CO) (cm^{-1})
PPN[$H_2CoRu_3(CO)_{12}$]	red	− 18.76	–	2077w, 2067w, 2033s, 2025s, 2003vs, 1995sh, 1960m, 1945sh, 1840w, 1824m, 1808m (THF)
$FeCo_2(NH)(CO)_9$	brown	[a]	3357	2103w, 2060s, 2046s, 2037s, 2024w, 1984m, 1976m (hexane)
$H_2Ru_3(NH)(CO)_9$	yellow	− 17.52, [a]	3362	2116m, 2080s, 2055s, 2046s, 2011s, 2001s, 1989m, 1960vw (hexane)
$CoRu_3N(CO)_{12}$	red	–	–	2074s, 2051s, 2027s, 2010w (hexane)

[a] N–H proton not observed.

the reaction of $[Co(CO)_4]^-$ and $Ru_3(CO)_{12}$, a reaction that is cleanly reversed by addition of CO. It was not surprising to find that the reaction of $[CoRu_3(CO)_{13}]^-$ with NO^+ (eq. 6) also leads mainly to fragmentation. At −78°C this fragmentation reaction is clean, however, as the temperature is raised an increased yield of the byproduct $CoRu_3N(CO)_{12}$ is found. The new nitrido cluster has been characterized by elemental and mass spectral analysis and infrared spectroscopy. It is isoelectronic with $HFe_4N(CO)_{12}$ [3] and $Fe_4N(CO)_{11}(NO)$ [3] both of which have "butterfly" metal frameworks with a μ_4-nitrogen atom. Analogous to these and all other $M_4X(CO)_{12}$ (X = C [23] or N) butterfly clusters, $CoRu_3N(CO)_{12}$ contains no bridging CO's. We suggest that $CoRu_3N(CO)_{12}$ has the structure shown in II, but we do not known whether the cobalt is located in the wing-tip or body position of the cluster.



(II)

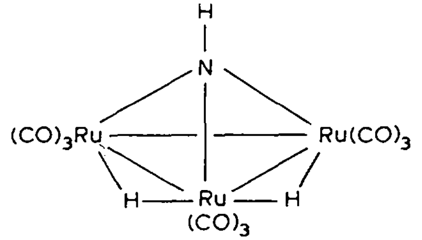
$[H_2CoRu_3(CO)_{12}]^-$. In an attempt to reduce products that arise from fragmentation we prepared the new cluster $[H_2CoRu_3(CO)_{12}]^-$ by the reaction of $[CoRu_3(CO)_{13}]^-$ with H_2 (eq. 8). This cluster was characterized by elemental

$$[CoRu_3(CO)_{13}]^- + H_2 \rightarrow CO + [H_2CoRu_3(CO)_{12}]^- \qquad (8)$$

analysis, infrared and ^1H NMR spectroscopy, as well as by its simple conversion upon protonation to $H_3CoRu_3(CO)_{12}$ which has been reported [24]. The solution infrared spectrum contains at least three absorbances in the bridging carbonyl region, suggesting the structure of $[H_2CoRu_3(CO)_{12}]^-$ is complex and probably exists as a mixture of isomers. From the ^1H NMR study of $H_3CoRu_3(CO)_{12}$ two isomers were found to be present, so it is not surprising that such is the case with its conjugate base.

$H_2Ru_3(NH)(CO)_9$. The reaction of $[H_2CoRu_3(CO)_{12}]^-$ with NO^+ also leads to substantial fragmentation and no $CoRu_3N(CO)_{12}$ is observed. The only cobalt products are $Co(CO)_3(NO)$ and $H_3CoRu_3(CO)_{12}$, both formed in low yield, while the major Ru product is $Ru_3(CO)_{12}$ with small amounts of $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$, $HRu_3(CO)_{10}(NO)$, and the new imido cluster $H_2Ru_3(NH)(CO)_9$. Although it is formed in very low yield, characterization of $H_2Ru_3(NH)(CO)_9$ was straightforward because of the large number of closely related $H_2Ru_3(\mu_3\text{-}X)(CO)_9$ compounds known. The infrared spectrum in the carbonyl region and the chemical shift of the bridging hydrogens are very similar to $H_2Ru_3(NOCH_3)(CO)_9$ [25], and the ν(N–H) was observed at 3362 cm^{-1}, suggesting structure III.

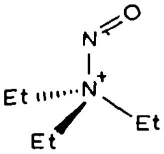
Modification of the reactivity of NO^+. There are many undesirable aspects of NO^+ that make it a less than ideal reagent for nitrosylations. First, NO^+ is incompatible with several valuable solvents, most notably THF. Second, NO^+ often is more effective as an oxidant as shown in eq. 9, in which no nitrosyl containing product is formed [26,27].



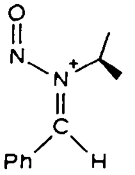
(III)

$$Mn_2(CO)_{10} + 2NO^+ \xrightarrow{CH_3CN} [Mn(CO)_5(CH_3CN)]^+ \tag{9}$$

We were interested in developing a method that would reduce the likelihood of oxidation, yet still allow the nitrosylations to occur at lower temperatures. Stabilization of NO^+ with an electron pair donor should reduce the oxidizing tendency. Diazald [28] and nitrous acid [29] are two nitrosylating reagents that make use of this approach. Nitrosyl chloride also has demonstrated value for this purpose [30]. The two reagents were chosen to do this and maintain an overall positive charge to promote the desired nitrosylation. These were triethylamine and *N*-t-butylbenzaldimine, the former generates the *N*-nitrosoammonium ion [31] (IV) and the latter forms the *N*-nitrosoiminium ion [32] (V). Since little at all is known about the



(IV)



(V)

TABLE 5

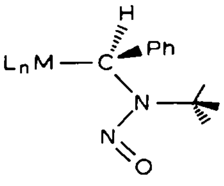
COMPARISON OF CONDITIONS FOR NITROSYLATIONS OF CARBONYLMETALLATES

Reactant	NO^+ source	Product (yield)
PPN[Mn(CO)$_5$]	NO^+	Mn$_2$(CO)$_{10}$ [a]
PPN[Mn(CO)$_5$]	NO^+/Et$_3$N	Mn$_2$(CO)$_{10}$ [a]
PPN[Mn(CO)$_5$]	NO^+/NTBB	Mn$_2$(CO)$_{10}$ (98%) [b]
PPN[Mn(CO)$_5$]	NO^+/NTBB/ − 78°C	Mn$_2$(CO)$_{10}$ (95%) [b]
PPN[Fe(CO)$_3$(NO)]	NO^+	– [c]
PPN[Fe(CO)$_3$(NO)]	NO^+/Et$_3$N	Fe(CO)$_2$(NO)$_2$ (65%) [b]
PPN[Fe(CO)$_3$(NO)]	NO^+/NTBB	Fe(CO)$_2$(NO)$_2$(92%) [b]
PPN[Co(CO)$_4$]	NO^+/Et$_3$N	Co(CO)$_3$(NO) [a]
PPN[Co(CO)$_4$]	NO^+/NTBB	Co(CO)$_3$(NO) [a]
K[CpMo(CO)$_3$]	NO^+/Et$_3$N	CpMo(CO)$_2$(NO) (79%) [d]
K[CpMo(CO)$_3$]	NO^+/NTBB	[CpMo(CO)$_3$]$_2$ [e]
K[CpFe(CO)$_2$]	NO^+/NTBB	[CpFe(CO)$_2$]$_2$ [f]
PPN[Mn(CO)$_2$(NO)$_2$]	NO^+/Et$_3$N	– [c]
PPN[Mn(CO)$_2$(NO)$_2$]	NO^+/NTBB	– [c]

[a] Only product observed. [b] Yield determined by quantitative infrared spectroscopy. [c] No infrared absorbances observed between 1600–2200 cm^{-1}. [d] Sublimed yield. [e] Product formed only after solvent evaporation; intermediate is proposed to be an alkyl complex (see text). [f] Alkyl complex initially formed, followed by rapid conversion to dimer.

reactivity of these ions, we began our work with the following series of mononuclear carbonylmetallates, [Co(CO)$_4$]$^-$, [Fe(CO)$_3$(NO)]$^-$, [Mn(CO)$_5$]$^-$, [Mo(η^5-C$_5$H$_5$)(CO)$_3$]$^-$, [Fe(η^5-C$_5$H$_5$)(CO)$_2$]$^-$, and [Mn(CO)$_2$(NO)$_2$]$^-$. The first advantage of the use of the nitrogen bases was that THF was not noticeably decomposed by the *N*-nitroso reagents. The general procedure involves mixing the nitrogen base with THF and adding this solution to the NOPF$_6$ to give a clear, pale yellow solution. The carbonylmetallate, dissolved in THF, is then added to this solution. Table 5 summarizes the reactions and conditions studied. It can be seen in several cases that decomposition results when NO^+ itself is used for the reaction, but that addition of the nitrogen base allows the isolation of reasonable yields of product.

The strategy behind the use of Et$_3$N was simply to have a good leaving group stabilizing the NO^+. With NTBB, however, we felt that nucleophilic attack at the imine carbon would be likely, generating structure VI shown below. Nucleophiles such as acetate are known to attack *N*-nitrosoiminium ions at the imine carbon [32]. Migration of the NO to the metal and subsequent elimination of the imine would lead to the desired product. When the cyclopentadienyl carbonylmetallates, [CpMo(CO)$_3$]$^-$ and [CpFe(CO)$_2$]$^-$, were treated with NTBB intermediate species were observed that have IR absorptions characteristic of CpMo(CO)$_3$R and



(VI)

$CpFe(CO)_2R$, where $R = CR_2NR'_2$ [33–35]. When $R' = CH_3$ these aminoalkyl complexes were found to be reasonably stable unlike the intermediates observed here, which decompose to the dimers $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$ and the free imine.

Although the reactions of the carbonylmetallates with NTBB are interesting because they may proceed via an intermediate alkyl, this reagent does not offer enough benefits over the triethylamine system to warrant further use.

Supplementary material available: See NAPS document no. 04073 for 11 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. $1.50 for postage of any microfiche orders.

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16 The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2(F_0)$. The unweighted and weighted residuals are defined as $R = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$ and $R_w = [(\Sigma w(|F_0| - |F_c|))^2/(\Sigma w|F_0|)^2]^{1/2}$. The error in an observation of unit weight is $[\Sigma w(|F_0| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the numbers of observations and variables, respectively.

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