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NITROSYL DERIVATIVES OF TRICOBALTCARBON CLUSTERS

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Summary

The nitrosyl clusters PPN[$YCCo_3(CO)_7(NO)$] (Y = Me, Ph, COOH, $(C_5H_5)Fe(C_5H_4)$) have been prepared in high yield from the reaction of $YCCo_3(CO)_9$ with PPN(NO_2) in THF, acetone or acetonitrile. Spectroscopic evidence indicates the structure of the nitrosyl anions is derived from that of $YCCo_3(CO)_9$ by the replacement of two CO ligands on one cobalt atom by a linear, terminal nitrosyl group. The nitrosyl metallates are extremely sensitive to oxidation and attempts to protonate the anions resulted in the reformation of the parent $YCCo_3(CO)_9$ molecules. The oxidative electrochemistry of the ferrocene complex, PPN[$(C_5H_5)Fe(C_5H_4)CCo_3(CO)_7(NO)$] is also discussed.

Introduction

The chemistry of nitrosyl coordination to transition metals has developed more slowly than the corresponding chemistry of the metal carbonyls [1] and, in metal cluster chemistry, the use of NO as a ligand is relatively rare [2]. Interest in this area of cluster research has been enlivened recently by the observations that cluster-bound NO can be *O*-methylated and *O*-protonated [3] or deoxygenated to yield nitrido derivatives [4]. It is also found that NO substitution will activate the cluster product towards donor ligands [5]. Three common modes of coordination of NO can be recognised in nitrosyl clusters [5–16]. In the first, NO binds to the transition metal in a linear, terminal fashion. The second sees one or more nitrosyl ligands bridging a metal–metal bond while in the third, the ligand acts as a bridge between the wingtip elements of a butterfly arrangement of metal atoms, an interaction not supported by metal–metal bonding. In all three bonding possibilities, the NO molecule can formally be regarded as a three electron donor to the cluster moiety. The traditional routes to nitrosylation, using NO gas or a source of NO^+ [17] have recently been augmented by the discovery [6,7] that bis(triphenylphosphine)nitrogen(+1) nitrite, PPN(NO_2), offers an effective alternative nitrosylating agent for metal carbonyl complexes, with nitrosyl coordination being accompanied by loss of CO_2.

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Previous attempts [18] to nitrosylate the tricobaltcarbon clusters, $YCCo_3(CO)_9$, using either NO gas or NO^+ salts did not result in the isolation of the expected $[YCCo_3(CO)_8(NO)]^+$ species. These observations may reflect the difficulties inherent in controlling the reactivity of the nitrosylating agent [19,20] as there would seem to be no a priori reason for the expected product not to exist. This paper reports the reaction of a number of tricobaltcarbon clusters with $PPN(NO_2)$ leading to the formation of the alternative, 48-electron nitrosyl derivatives, $[YCCo_3(CO)_7(NO)]^-$ [21].

Experimental

The tricobaltcarbon clusters $YCCo_3(CO)_9$ (Y = Me, Ph, COOH [22], (C_5H_5)-$Fe(C_5H_4)$ (Fc) [23]) were prepared by literature methods. $PPN(NO_2)$ was prepared by salt metathesis between PPNCl and $NaNO_2$ using the method of Martinson and Songstad [24]. Trifluoro- and trichloroacetic acids (BDH) were used as received. All reactions and manipulations were carried out in an argon atmosphere with rigorous exclusion of molecular oxygen. Solvents, purified and dried as described previously [25], were degassed before use by successive freeze-thaw cycles in vacuo. Conventional dc polarograms and cyclic voltammograms were recorded in acetone on Princeton Applied Research equipment [25]. The reference electrode was a Ag/AgCl electrode using saturated LiCl in acetone, separated from the solution by a salt bridge containing 0.1 *M* Et_4NClO_4 in acetone. The reference electrode was calibrated using the one electron oxidation wave of ferrocene (0.63 V in acetone/Et_4NClO_4) as an internal reference. Solutions were approximately 10^{-3} *M* in electroactive species and 0.1 *M* in Et_4NClO_4 as supporting electrolyte.

Preparations of PPN[YCCo$_3$(CO)$_7$(NO)]

Typically, $PPN(NO_2)$ (70 mg, 0.12 mmol) was added to $MeCCo_3(CO)_9$ (50 mg, 0.11 mmol) in THF, acetone or acetonitrile (30 cm^3). The solution changed colour from purple to brown and rapid gas evolution was observed as the $PPN(NO_2)$ completely dissolved. Infrared spectra (2200–1600 cm^{-1}) of the solution showed the complete disappearance of bands attributable to $MeCCo_3(CO)_9$ following $PPN(NO_2)$ dissolution. Solvent was removed under vacuum, the black, tarry residue dissolved in a minimum of Et_2O and the resulting solution was slowly filtered into 50 cm^3 of rapidly stirred hexane. Filtration of the resulting product gave bis(triphenylphosphine)nitrogen(+1) heptacarbonyl-μ_3-ethylidine-nitrosyltricobaltate(*Co–Co*). $PPN[MeCCo_3(CO)_7(NO)]$, as a brown amorphous powder (110 mg, 0.12 mmol, > 95%); Found: C, 54.19; H, 4.31; $C_{45}H_{33}O_8N_2P_2Co_3$ calcd.: C, 54.22; H, 3.31%.

Other nitrosyl cluster anions were prepared similarly and their spectroscopic properties are detailed in Table 1. All of the products were soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, benzene, ether or acetone but insoluble in CCl_4 or hexane. The anions proved to be extremely unstable towards aerial oxidation. Exposure of solutions, tars or solid samples to the atmosphere led to rapid and complete decomposition. IR spectra of the decomposition products showed bands at 1885 and 1880 cm^{-1}. Extraction of a solid sample of the decomposition product with CH_2Cl_2 led to the isolation of $PPN[Co(CO)_4]$ (ν(CO) 1885 cm^{-1}) [26].

Conductometric titration of MeCCo$_3$(CO)$_9$ with PPN(NO$_2$)

$MeCCo_3(CO)_9$ (25.46 mg, 0.056 mmol) in acetone (50.00 cm^3) was degassed in a

Schlenk tube equipped with a magnetic stirring bar, a self-equilibrating dropping funnel and a conductivity cell attached as a sidearm. A solution of PPN(NO_2) (160.60 mg, 0.275 mmol) in acetone (10 cm^3) was degassed separately. Aliquots of PPN(NO_2) solution (0.2 cm^3) were transferred to the cluster solution via a rubber septum cap, using a gas-tight syringe. The resulting solution was stirred in vacuo and, if necessary, the solution volume was adjusted to 50.00 cm^3 by the addition of further acetone. Solution resistance was measured after stirring for a further 5 min. An endpoint was observed after the addition of 1 mol of PPN(NO_2) per mol of $MeCCo_3(CO)_9$. The molar conductivity of the solution at the endpoint was commensurate with the presence of a 1 : 1 electrolyte (Λ_M 150 Ω^{-1} cm^2 mol^{-1}). An IR spectrum of the solution, recorded after the addition of the final aliquot of PPN(NO_2) showed only the ν(CO) bands expected for the product nitrosylcarbonyl anion with no band due to $Co(CO)_4^-$.

Reactions of PPN[$YCCo_3(CO)_7(NO)$] with excess CX_3COOH (X = F, Cl)

CCl_3COOH (0.1 cm^3) was added to PPN[$YCCo_3(CO)_7(NO)$] (30 mg, 0.06 mmol) in CH_2Cl_2 (10 cm^3). Gas evolution was immediately observed and the solution turned from brown to purple over a period of 5 min. The solvent was removed in vacuo and the residue extracted with hexane. $MeCCo_3(CO)_9$ (20 mg, 0.04 mmol) was recovered by evaporation of the hexane extracts.

Similar reactions of other PPN[$YCCo_3(CO)_7(NO)$] complexes with either CCl_3COOH or CF_3COOH also led to the recovery of the corresponding nonacarbonyl complexes.

Results and discussion

The reaction of a variety of tricobaltcarbon clusters, $YCCo_3(CO)_9$, with PPN(NO_2) under rigourously anaerobic conditions gives the nitrosyl complexes PPN[$YCCo_3(CO)_7(NO)$] in high yield (> 90%) according to eq. 1.

$$YCCo_3(CO)_9 + PPN(NO_2) \rightarrow PPN[YCCo_3(CO)_7(NO)] + CO + CO_2 \quad (1)$$

The stoichiometry of the reaction is confirmed by the results of a conductiometric titration of $MeCCo_3(CO)_9$ with PPN(NO_2). The resulting PPN^+ salts of the nitrosyl anions are obtained as brown/black amorphous powders and are extremely sensitive to aerial oxidation. Decomposition in air leads to the formation of PPN[$Co(CO)_4$]

TABLE 1

INFRARED SPECTRA (cm^{-1}) OF PPN[$YCCo_3(CO)_7(NO)$] DERIVATIVES[a,b]

Apical group (Y)	ν(CO)					ν(NO)
Fc[c]	2035s	1965vs	1951vs	1930m	1857m	1715ms
Me[d]	2037s	1965vs	1953vs	1931m	1864m	1716ms
Ph	2039s	1972vs	1952vs	1935m	1870m	1724ms
COOH	2047s	1980vs	1970vs			1740ms

[a] Recorded in THF. [b] A small peak at 1590 cm^{-1} due to the PPN^+ cation was observed in all spectra. [c] ^1H NMR ($CDCl_3$) 7.50–7.30 (m), 4.2 (br. m, Fc) ppm. [d] ^1H NMR (CD_3CN) 7.40–7.30 (m), 3.58 (s, Me) ppm.

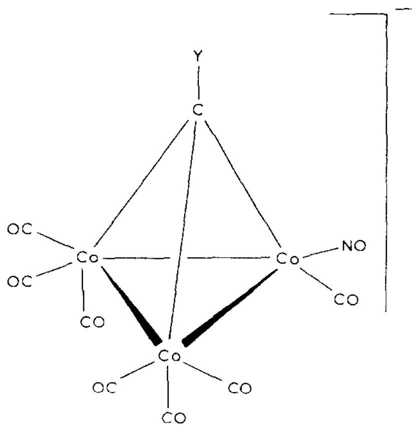

Fig. 1. Probable structure of the $[YCCo_3(CO)_7(NO)]^-$ anions.

and other, as yet uncharacterised products. Attempts to obtain suitable single crystals for X-ray diffraction analysis have been unsuccessful and the compounds were characterised on the basis of analytical and spectroscopic data (Table 1).

The IR spectra of the compounds in THF generally exhibited 5 bands in the CO stretching region. The four highest frequency bands can be readily identified as the vibrations of terminal carbonyl groups of the tricobaltcarbon clusters [27], while the low frequency bands (1870–1857 cm^{-1}) can be assigned to the terminal carbonyl groups bound to the nitrosyl substituted cobalt atoms. A terminal carbonyl vibration of similar frequency was found in the anion $[Os_3(CO)_{10}(NO)]^-$ [7]. The appearance of NO stretching vibrations for all compounds in the range 1715–1740 cm^{-1} demonstrated that the NO ligands also bind in a linear, terminal fashion [28]. The variation in energy of the carbonyl and nitrosyl stretching vibrations with the nature of the substituent on the capping carbyne atom of the Co_3C unit, confirms that the structural integrity of the cluster unit is maintained following nitrosyl substitution. The highest frequency $\nu(CO)$ bands in the nitrosyl anions are shifted ~ 60 cm^{-1} to lower energy in comparison with the corresponding vibrations in the parent nonacarbonyls. This indicates that the negative charge of the metallate anion is effectively delocalised over the cluster unit. It is interesting to note that reduction of tricobaltcarbon clusters to their radical anions $YCCo_3(CO)_9^{-\cdot}$ causes a comparable shift to low frequency of the carbonyl stretching vibrations [29]. The ^1H NMR spectra of the methyl and ferrocene capped clusters showed the expected resonances from the protons of the respective apical substituents, providing further evidence that the $YCCo_3$ unit remains intact in the nitrosyl derivatives. Spectral evidence therefore suggests that the nitrosyl anions have the structure shown in Fig. 1, although the relative placement of the NO and CO ligands on the unique cobalt atom cannot be specified with certainty.

Attempts to protonate the nitrosyl anions using excess trihaloacetic acids led, in all cases, to gas evolution and the recovery of the parent nonacarbonyl clusters, $YCCo_3(CO)_9$, in less than quantitative yields. It is probable that protonation of the nitrosyl anion occurs initially to give a hydrido derivative, $YCCo_3(CO)_7H(NO)$, which, in the presence of adventitious CO, reforms the parent nonacarbonyl complex $YCCo_3(CO)_9$. The ruthenium hydrido-nitrosyl cluster, $Ru_3(CO)_{10}H(NO)$ decomposes similarly in the absence of air to produce $Ru_3(CO)_{12}$ [15]. Comparable displacement of coordinated nitric oxide by CO has been observed following protonation in mononuclear nitrosyl complexes and has been ascribed to initial electrophilic attack on an intermediate "bent" M–N–O group [30].

Previous investigations of the chemistry of tricobaltcarbon clusters capped by a ferrocene moiety [23] led to the isolation and characterisation of novel, mixed-valence ions of the type $[FcCCo_3(CO)_6L_3]^+$ (L = $P(OMe)_3$, $P(OPh)_3$) [31]. The observation of intervalence charge transfer in these oxidised species provided evidence for some degree of delocalisation between the potentially oxidisable Fc and Co_3C centres in the molecules. The preparation of the nitrosyl metallate $[FcCCo_3(CO)_7(NO)]^-$ offered the possibility of obtaining a unique example of a mixed-valence complex without formal electronic charge, via the one electron oxidation of the nitrosyl anion. Cyclic voltammetry at platinum of an acetone solution of $PPN[FcCCo_3(CO)_7(NO)]$ showed two well defined oxidation waves at 0.20 and 0.76 V vs. Ag/AgCl respectively, (Fig. 2). Both waves were completely irreversible at scan rates up to 500 mV s^{-1}. Comparison with the oxidation behaviour of the parent nonacarbonyl [23] allows assignment of the oxidation wave at the more positive potential to the oxidation of the ferrocene moiety. Hence the wave at 0.20 V must correspond to the irreversible oxidation of the tricobalt carbon centre. An additional oxidation process is observed at 0.4 V vs. Ag/AgCl and remains if the potential is switched before the second oxidation process of the nitrosyl complex. This additional wave may be assigned to the oxidation of $Co(CO)_4^-$ [32] which may be identified as a product of the decomposition of the neutral complex $FcCCo_3(CO)_7(NO)$. The oxidation processes may be summarised by eq. 2.

$$FcCCo_3(CO)_7(NO)^- \xrightarrow{0.20\ V} FcCCo_3(CO)_7(NO) \xrightarrow{0.76\ V} Fc^+CCo_3(CO)_7(NO) \quad (2)$$

Clearly the facile, irreversible oxidation of the tricobaltcarbon centre precludes the observation of the normal reversible oxidation [23] of the ferrocene substituent and obviates the possibility of isolating the hoped for, neutral, nitrosyl derivative. The

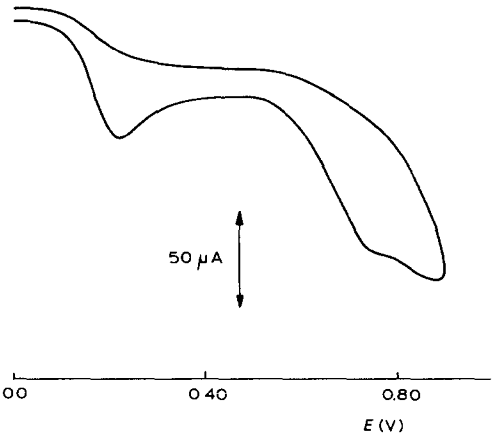

Fig. 2. Cyclic voltammogram of 10^{-3} *M* $PPN[FcCCo_3(CO)_7(NO)]$ measured in acetone containing 0.1 *M* Et_4NClO_4 at 293 K vs. Ag/AgCl.

low stability of the nitrosyl anions towards chemical oxidation can be rationalised similarly. In the light of these observations, the electrochemistry of these complexes was not investigated further.

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