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ATOM-TRANSFER REDOX REACTIONS OF NITRITE ANION WITH TRANSITION METAL CARBONYL CATIONS

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Summary

The reactions of several carbonyl cations with bis(triphenylphosphine)imminium nitrite under aprotic conditions have been studied using acetone as solvent. The trigonal-bipyramidal iron(0) and cobalt(I) cations $[Fe(N_2C_6H_4COCH_3\text{-}p)(CO)_2(PPh_3)_2]^+$, $[Fe(NO)(CO)_2(PPh_3)_2]^+$, $[Co(CO)_3(PPh_3)_2]^+$ and $[Co(CO)_2(P(Bu\text{-}n)_3)_2]^+$ yielded four-coordinate iron(–II) and cobalt(–I) nitrosyl complexes $Fe(NO)(N_2C_6H_4COCH_3\text{-}p)(CO)(PPh_3)$, $Fe(NO)_2(CO)(PPh_3)$, $Fe(NO)_2(PPh_3)_2$, $Co(NO)(CO)_2(PPh_3)$ and $Co(NO)(CO)_2(P(Bu\text{-}n)_3)$ via a procedure which is much simpler than previous methods. The reaction involves an atom-transfer redox between nitrite and coordinated CO to yield the coordinated nitrosyl ligand and CO_2. The related cation $[Co(CO)_3(P(NMe_2)_3)_2]^+$ did not react. The other cations investigated underwent decomposition and/or gave non-nitrosyl products with the exception of $[Co(\eta\text{-}C_5H_5)(C_3F_7)(CO)(PPh_3)]^+$ which yielded an unstable blue nitrosyl which could not be characterised. A modification of the procedure employing $Na^{15}NO_2$ in the presence of a catalytic amount of crown ether was shown to be a very simple method for the preparation of ^{15}N-labelled nitrosyls. The analogous reaction with arenediazotate anion did not lead to arenediazo complexes.

Introduction

In a recent note Gladfelter and co-workers [1] reported that bis(triphenylphosphine)imminium nitrite, $[PPN]NO_2$ [2], is an efficient reagent for the preparation of transition metal nitrosylcarbonyl complexes under neutral aprotic conditions. We here describe the results of a related study carried out in these laboratories [3].

Results and discussion

The cationic trigonal-bipyramidal arenediazoiron(0) complexes $[Fe(N_2Ar)(CO)_2(PPh_3)_2]BF_4$ (I) react with [PPN]X (X = Cl, Br, N_3 etc.) in acetone at room temperature to yield five-coordinate neutral iron(0) complexes of the type

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$FeX(N_2Ar)(CO)(PPh_3)_2$ (II) [4]. When $[PPN]NO_2$ was employed in this reaction, (I, $Ar = C_6H_4COCH_3$-*p*), the expected five-coordinate nitritoiron(0) complex (II, $X = NO_2$) was not observed. Instead the product was the four-coordinate nitrosylarenediazoiron(−II) complex $Fe(NO)(N_2C_6H_4COCH_3\text{-}p)(CO)(PPh_3)$ (III) which we had previously prepared by a different route [5]. Complex III was isolated in ca. 73% yield and is formed via an atom-transfer redox process [6] between nitrite anion and coordinated CO (eq. 1).

$$[Fe(N_2Ar(CO)_2(PPh_3)_2]^+ + NO_2^- \rightarrow Fe(NO)(N_2Ar)(CO)(PPh_3) + PPh_3 + CO_2 \quad (1)$$

That nitrite oxygen is transferred exclusively to CO and not to PPh_3 [7] was shown by trapping the evolved CO_2 as $BaCO_3$ (74%) and the TLC detection of PPh_3 (but not PPh_3O) in the crude reaction product. The reaction provides much more convenient access to complexes of type III than our previous method: reaction of $[Fe(NO)(CO)_3]^-$ with $[ArN_2]^+$ at −70°C, followed by addition of PPh_3.

The cationic iron(0) nitrosyl complex $[Fe(NO)(CO)_2(PPh_3)_2]PF_6$ (IV) undergoes an analogous reaction with $[PPN]NO_2$. Investigation of the crude product by IR and TLC showed it to contain approximately equivalent amounts of $Fe(NO)_2(CO)(PPh_3)$ (V) and $Fe(NO)_2(PPh_3)_2$ (VI) as well as PPh_3. However dry column chromatography of the mixture yielded VI as the major product (43%) and 11% of V. This reaction has also been investigated by Gladfelter [1] who, however, reports exclusive formation of the monocarbonyl complex V under his experimental conditions (room temperature, acetonitrile). The origin of this difference in results is not clear.

In an attempt to extend this synthetic method to the preparation of novel iron nitrosyl complexes we have investigated the reactions of $[PPN]NO_2$ with three other cationic iron carbonyl complexes: $[Fe(\eta\text{-}C_5H_5)(CO)_3]PF_6$ (VII), $[Fe(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]PF_6$ (VIII) and $[Fe(NO)(CO)_2(\eta^4\text{-}Ph_4C_4)]PF_6$ (IX). All three complexes reacted rapidly with $[PPN]NO_2$ under our conditions but the products were not those which would be predicted on the basis of our earlier results. Complex VII yielded the neutral dimer $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ as the only carbonyl-containing product (ca. 30%). The latter was also produced in the reaction of VIII with $[PPN]NO_2$ (ca. 40%) but the nitrosyl complex $Fe(NO)_2(PPh_3)_2$ (VI) was also formed (ca. 30%). The mode of formation of VI in this reaction is unclear but may involve decomposition of an unstable nitrosyl complex derived from VIII. Complex IX gave a polynuclear nitrito complex $[Fe(NO_2)(NO)(\eta^4\text{-}Ph_4C_4]_n$ which is described in more detail elsewhere [8].

More encouraging results were obtained with the cationic cobalt(I) carbonyl complexes $[Co(CO)_3(PPh_3)_2]PF_6$ (X) and $[Co(CO)_3(P(n\text{-}Bu_3)_2][Co(CO)_4]$ (XI) in which the cation is isostructural and isoelectronic with I and IV and which reacted with $[PPN]NO_2$ in an analogous fashion (eq. 2).

$$\underset{(X,\ XI)}{[Co(CO)_3L_2]^+} + NO_2^- \rightarrow \underset{(XII,\ L = PPh_3;\ XIII,\ L = P(n\text{-}Bu)_3)}{Co(NO)(CO)_2L} + L + CO_2 \quad (2)$$

The cobalt(−I) nitrosyl complexes VII and XIII were isolated in ca. 70% yield and an equivalent amount of CO_2 was trapped as $BaCO_3$. Complexes XII and XIII have been previously prepared by the reaction of the appropriate ligand with the air-sensitive $Co(NO)(CO)_3$ [9,10] and the ease of preparation of cations X and XI

[11,12] makes the present synthesis an attractive alternative. Surprisingly the related complex $[Co(CO)_3(P(NMe_2)_3)][Co(CO)_4]$ (XIV) failed to react with $[PPN]NO_2$ and was recovered unchanged. It may be that the electron-releasing character of the phosphine NMe_2 substituents stabilise the carbonyl cation XIV against nucleophilic attack by NO_2^-. In order to compare the efficacy of $[PPN]NO_2$ as a nitrosylating agent with that of $NaNO_2$, complex X was treated with finely powdered $NaNO_2$ in acetone at room temperature. No reaction ensued and both X and the insoluble nitrate salt were quantitatively recovered. However, addition of a catalytic amount (0.1 equiv.) of dibenzo-18-crown-6 to the reaction-mixture caused the nitrosylation to proceed and complex XII was formed in ca. 60% yield. Using $Na^{15}NO_2$ in place of $NaNO_2$ allowed the preparation of the isotopically labelled nitrosyl XII in similar yield ($\bar{\nu}(^{15}NO)$ 1724 cm^{-1}). This modification of the nitrite reaction should prove a useful method of generating isotopically-labelled nitrosyl complexes directly from commercially available labelled nitrite salts in aprotic media. (The employment of standard phase-transfer conditions for this reaction would be an even more convenient alternative and merits further investigation). The cobalt(III) carbonyl cation $[Co(\eta\text{-}C_5H_5)(C_3F_7)(CO)(PPh_3)]PF_6$ (XV) reacted slowly with $[PPN]NO_2$ at room temperature and more rapidly at reflux to yield an unstable air-sensitive deep blue oil which exhibited a strong absorbtion at 1845 cm^{-1} in its IR spectrum. This may be the presently unknown cobalt(I) nitrosyl complex $Co(\eta\text{-}C_5H_5)(C_3F_7)(NO)$ (XVI) but its instability prevented further characterisation *.

Gladfelter et al. proposed that nitrosylation by nitrite anion under aprotic conditions proceeds via initial nucleophilic attack at carbonyl carbon [1]. This is also the most plausible route for the cobalt carbonyl cations discussed here, X and XI, since the alternative, attack of nitrite at the metal centre, would involve an unfavourable 20-electron configuration at cobalt. The situation is less clear-cut for the arenediazo and nitrosyl cations I and IV. Both $[NO]^+$ and $[ArN_2]^+$ ligands can function as two-electron sinks via conversion to formal $[NO]^-$ and $[ArN_2]^-$, respectively, thus potentially enabling an incoming nitrite ligand to bond directly to the metal centre. Oxygen transfer from metal-coordinated nitrite to coordinated CO has, inter alia, been well documented for the complex $Ru(NO_2)_2(CO)_2(PPh_3)_2$ [7]. A mechanistic study of the carbonyl cation/nitrite anion system is clearly desirable in order to elucidate whether the same reaction pathway is followed in all cases.

Formal replacement of nitrite by arenediazotate anion, $[ArN_2O]^-$, in the reactions described above would provide a potential new route to arenediazo complexes (eq. 3). In order to investigate this possibility we attempted to prepare the $[PPN]^+$ salt of

$$[L_nM(CO)]^+ + [ArN_2O]^- \rightarrow L_{n-1}M(N_2Ar) + L + CO_2 \qquad (3)$$

the *p*-nitrophenyldiazotate anion $[PPN][p\text{-}NO_2C_6H_4N_2O]$ (XVII). However mixing of aqueous solutions of [PPN]Cl and $Na[p\text{-}NO_2C_6H_4N_2O]$ (XVIII) [13] resulted in gas evolution and the formation of intractable green tarry materials. The sodium salt XVIII reacted rapidly with $Fe(CO)_5$ in dry tetrahydrofuran at room temperature (conditions which lead to $[PPN][Fe(NO)(CO)_3]$ with $[PPN]NO_2$ [1]) but no carbonyl-containing products were formed. While XVIII also reacted with the cobalt

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* *Note added in proof.* The formation of $[Fe(NO)(CO)_3]^-$ from $Fe(CO)_5$ and $NaNO_2$ under phase-transfer conditions has been described by E.V. Dehmlov, Z. Naturforsch. B, 37 (1982) 1216.

carbonyl cations XII and XIII in acetone at room temperature the products were not arenediazo complexes but the known species $[Co(CO)_2(PPh_3)]_3$ (XXIX) [14] and $[Co(CO)_3(P(n\text{-}Bu)_3)]_2$ (XXX) [12] respectively.

Experimental

The complexes I [15], IV [16], V, VI [17], VII [18], VIII [19], IX [20], X [11], XI [12], XIV [21], XV [22], as well as $[PPN]NO_2$ [2] and $Na[p\text{-}NO_2C_6H_4N_2O]$ [13] were prepared by the literature methods. All other reagents and solvents were commercially available and were used as received. IR spectra were recorded on a Perkin–Elmer 257 spectrophotometer. Microanalyses were carried out by the staff of the Microanalytical Laboratory of University College, Cork and are summarised in Table 1. The IR spectra of all compounds described were identical with the published data.

Reaction of $[Fe(N_2C_6H_4COCH_3\text{-}p)(CO)_2(PPh_3)_2]BF_4$ *(I) with* $[PPN]NO_2$

In a 250 ml 3-necked round-bottom flask (fitted with a nitrogen inlet, magnetic stirring bar, pressure-equalised dropping funnel and a gas outlet connected to a train of three Dreschel bottles containing freshly-prepared aqueous $Ba(OH)_2$ solution) was placed a solution of I (2.46 g, 2.88 mmol) in 70 ml of acetone. A solution of $[PPN]NO_2$ (1.59 g, 2.88 mmol) was placed in the dropping-funnel and the system was purged with N_2. The $[PPN]NO_2$ solution was added dropwise to the stirred solution of I while a stream of N_2 through the apparatus was maintained. Gas was evolved and the solution turned deep brown. After 1 h the solvent was removed in vacuo. TLC analysis of the residue against authentic materials showed the presence of II and PPh_3 but no PPh_3O. The crude product was recrystallised from 1/1 ether/pentane at −78°C to yield analytically pure II (1.10 g, 73%). The solutions in the $Ba(OH)_2$ traps were filtered and the combined precipitates dried in vacuo at 50°C to yield $BaCO_3$ (0.42 g, 74%).

Other reactions with $[PPN]NO_2$. The general procedure was as described above except that the crude products were purified by dry-column chromatography on neutral alumina. In the reaction of $[PPN]NO_2$ with $[Fe(NO)(CO)_2(PPh_3)_2][PF_6]$ (IV) (2.5 mmol scale) the IR spectrum of the crude product (cyclohexane solution) showed strong bands at 2010, 1764, 1723 and 1677 cm^{-1} compatible with a mixture of $Fe(NO)_2(CO)(PPh_3)$ (V) ($\bar{\nu}(CO)$ 2009, $\bar{\nu}(NO)$ 1764, 1722 cm^{-1} [17]) and

TABLE 1

MICROANALYTICAL DATA

Complex	Analysis (Found (calcd.) (%))		
	C	H	N
III	61.72 (61.97)	4.41 (4.24)	7.68 (8.03)
V	55.84 (56.19)	3.90 (3.72)	7.29 (6.90)
VI	67.21 (67.51)	5.21 (4.72)	4.19 (4.37)
XII	59.25 (58.98)	4.00 (3.71)	3.18 (3.44)
XIII	48.01 (48.42)	8.05 (7.84)	4.46 (4.03)
XXIX	64.05 (63.68)	3.86 (4.01)	
XXX	52.15 (51.82)	7.86 (7.57)	

$Fe(NO)_2(PPh_3)_2$ (VI) ($\bar{\nu}$(NO) 1724, 1678 cm^{-1} [17]). The relative intensities of the bands suggested approximately equal amounts of V and VI were present. Comparative TLC against authentic V and VI reinforced this conclusion. However dry-column chromatography of the crude mixture on neutral alumina eluting with 1/1 ether/pentane, yielded $Fe(NO)_2(PPh_3)_2$ (VI) (0.90 g, 43%) and only 0.11 g (11%) of V.

Reactions with $Na[p\text{-}NO_2C_6H_4N_2O]$ (XVIII)

(a) $[Co(CO)_3(PPh_3)_2]PF_6$ *(X).* Complex X (4.87 g, 6.0 mmol) in 150 ml acetone was treated portionwise under N_2 with solid $Na[p\text{-}NO_2C_6H_4N_2O]$ (XVIII) (1.12 g, 6.0 mmol). The solution became deep red and after a few minutes a red solid began to precipitate. After 1.5 h this was collected by filtration, washed with acetone and ether and dried in vacuo to yield $[Co(CO)_2(PPh_3)]_3$ (XXIX) (1.3 g, 57%).

(b) $[Co(CO)_3(P(n\text{-}Bu)_3)_2][Co(CO)_4]$ *(XI).* Complex XI (3.3 g, 4.6 mmol) was treated with the diazotate salt XVIII as described in (a) above. After 1 h the solution was concentrated to dryness in vacuo. The residue was dissolved in CH_2Cl_2, the solution was filtered through a short (5 × 5 cm) column of neutral alumina and diluted with hexane. Slow evaporation of the mixture yielded red-brown crystals $[Co(CO)_3(P(n\text{-}Bu)_3)_2]_2$ (XXX) (1.8 g, 54.5%).

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