were produced. After hydriding, an X-ray diffraction pattern of the product indicated the presence of FeTiH$_{\sim2}$, TiH$_{\sim2}$, FeTi, and Ti. The increased amount of residual hydrogen in the solid is undoubtedly due to the presence of the stable titanium hydride.

Upon departing from the single-phase region in the opposite direction, *i.e.,* that of higher iron content, there appears to be no significant effect other than a reduction in the amount of hydrogen sorbed as shown in Figure 5. The starting alloy was a two-phase mixture, Fe$_2$Ti and FeTi, having an overall composition of 60.5 wt % Fe and 39.5 wt % Ti. The isotherm A is essentially congruent with that obtained with FeTi, indicating little interaction between the two

phases or solid solubility of Fe in FeTi; an observation which is in accord with the known homogeneity range of FeTi. The amount of hydrogen actually sorbed is somewhat less than that expected from the proportionate amount of FeTi present in the alloy, which may be due to the mere physical presence of Fe$_2$Ti.

Reactivity of Mixed Carbonyl–Nitrosyl Complexes of Iron(0)

GIULIANO DOLCETTI,* LUIGI BUSETTO, and ANTONIO PALAZZI

Neutral complexes of the type FeX(NO)(CO)L$_2$ (L = (P(C$_6$H$_5$)$_3$ and X = N$_3$, SCN, CNO, CN, SeCN; L = P(CH$_3$)(C$_6$H$_5$)$_2$ and X = N$_3$, SCN) have been prepared from the cationic [Fe(NO)(CO)$_2$L$_2$]$^+$ complexes by reaction with the appropriate sodium salt. The formation of the azide complex FeN$_3$(NO)(CO)L$_2$ from the starting carbonyl cationic complexes is related to the stabilization of a six-coordinate transition state due to the nitrosyl ligand. The geometrical configuration of the neutral complexes is discussed on the basis of the ir and nmr spectra.

Introduction

The reactivity of nitrosyl complexes has recently received considerable attention.[1] The coordinated nitrosyl ligand has been found to be rather inert to displacement by electron-pair donors such as cyanide, hydroxide, and tertiary phosphines. This inertness to substitution is not found in the carbonyl case. Our interest in this field led us to study the reactivity of some cationic complexes in which both nitrosyl and carbonyl ligands are coordinated to the same metal.

Results and Discussion

We now report the preparation and the characterization of a series of new compounds of the type FeX(NO)(CO)L$_2$ (L = P(C$_6$H$_5$)$_3$ and X = N$_3$, SCN, CNO, CN, SeCN; L = P(CH$_3$)-(C$_6$H$_5$)$_2$ and X = N$_3$, SCN). The compounds are obtained by reaction of [Fe(NO)(CO)$_2$L]PF$_6$ recently reported by Johnson, *et al.,*[2,3] with the appropriate sodium salt.

$$[Fe(NO)(CO)_2L_2]^+ + X^- \rightarrow FeX(NO)(CO)L_2 + CO \qquad (1)$$
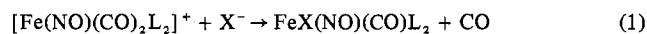
From a 50:50 water–acetone suspension of dicarbonylnitrosylbis(tertiary phosphine)iron(0) a vigorous effervescence, with gas evolution, occurs after addition of the salt. The product spontaneously precipitates from the reaction mixture as a microcrystalline, colored solid.

All the compounds are soluble in polar organic solvents such as acetone, acetonitrile, nitrobenzene, dichloromethane, and chloroform. However, they decompose rapidly in these solutions. For this reason it is essential to carry out the reactions in the presence of a large percentage of water to ensure rapid precipitation of the desired products, thus avoiding side reactions which lead to unidentified brown by-products. Reactions with LiCl, LiBr, and LiI in acetone-water lead only to the metathetical exchange of the hexafluorophosphate anion by chloride, bromide, and iodide, since the ir spectra are identical with these of the starting materials.[4]

All the members of the series are stable to the air in the solid state for months. The nature of FeX(NO)(CO)L$_2$ was established from elemental analyses (Table I), ir spectra, nmr spectra, and conductance measurements.

The ir spectra of the complexes (Table II) exhibit one ν(CO) stretching vibration in the range 1910–1930 cm^{-1} and one ν(NO) stretching vibration in the range 1670–1700 cm^{-1} consistent with the proposed formulation. The stretching vibrations for both the carbonyl and the nitrosyl groups are about 100 cm^{-1} lower than these of the parent iron(0) complex. Although the two limiting coordination forms of the NO group, NO$^+$ and NO$^-$, cannot be unequivocally distinguished on the basis of the ν(NO) frequency,[5] the appearance of the ν(NO) stretching vibration in the 1670–1700-cm^{-1} range, for neutral complexes, suggests that the nitrosyl ligand is acting as a formal three-electron donor (NO$^+$) and that the Fe–N–O arrangement is linear.

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(3) B. F. G. Johnson and J. A. Segal, *J. Organometal. Chem.,* 31, C79 (1971).

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Table I. Analytical Data and Physical Properties of the Compounds

	Color	Mp, °C (dec)	% calcd					% found				
			C	H	N	P	S	C	H	N	P	S
$Fe(N_3)(NO)(CO)(P(C_6H_5)_3)_2$	Red	117–120	64.33	4.56	8.00	9.04		64.80	4.40	8.21	9.14	
$Fe(N_3)(NO)(CO)(P(CH_3)(C_6H_5)_2)_2$	Orange-red	82–85	57.08	4.73	10.20	10.84		58.10	4.70	10.70	11.3	
$Fe(SCN)(NO)(CO)(P(C_6H_5)_3)_2$	Brown	145–148	65.10	4.28	3.78	8.75	4.56	65.70	4.30	4.01	8.92	4.50
$Fe(SCN)(NO)(CO)(P(CH_3)(C_6H_5)_2)_2$	Orange-brown	102–106	58.04	4.57	4.98	10.54	6.08	58.5	4.51	4.87	10.80	6.26
$Fe(CNO)(NO)(CO)(P(C_6H_5)_3)_2$	Orange		66.15	4.30	4.50	9.06		67.10	4.40	4.10	9.13	
$Fe(SeCN)(NO)(CO)(P(C_6H_5)_3)_2$	Brown	159–161	62.04	4.10	3.60	8.10		61.50	4.04	3.77	8.37	
$Fe(CN)(NO)(CO)(P(C_6H_5)_3)_2$	Dark brown		69.31	4.39	4.41	9.10		68.70	4.52	4.22	9.35	

Table II. Infrared Data (700–4000 cm^{-1}) for the Nitrosyl Complexes as Nujol Mulls

|	$\nu(CO)$, cm^{-1}	$\nu(NO)$, cm^{-1}
$[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]PF_6$	2051 s, 1995 vs	1792 vs
$Fe(N_3)(NO)(CO)(P(C_6H_5)_3)_2$	2060 vs ($\nu(N_3)$), 1910 vs	1680 vs
$Fe(N_3)(NO)(CO)(P(CH_3)(C_6H_5)_2)_2$ [a]	2035 vs ($\nu(N_3)$), 1915 vs	1685 vs
$Fe(SCN)(NO)(CO)(P(C_6H_5)_3)_2$	2090 s ($\nu(SCN)$), 1930 vs	1690 vs
$Fe(SCN)(NO)(CO)(P(CH_3)(C_6H_5)_2)_3$ [a]	2090 s ($\nu(SCN)$), 1925 vs	1700 vs
$Fe(SeCN)(NO)(CO)(P(C_6H_5)_3)_2$	2082 s ($\nu(SeCN)$), 1932 vs	1700 vs
$Fe(CNO)(NO)(CO)(P(C_6H_5)_3)_2$	2195 m ($\nu(CNO)$), 1910 vs	1670 vs
$Fe(CN)(NO)(CO)(P(C_6H_5)_3)_2$	2100 m ($\nu(CN)$), 1930 vs	1700 vs
$[Fe(NO)(diphos)(P(C_6H_5)_3)_2]PF_6$		1675 vs
$[Fe(NO)(di=phos)(P(C_6H_5)_3)_2]PF_6$		1730 vs

[a] As KBr pellets.

In this case and in contrast with the behavior exhibited by certain five-coordinate cobalt–nitrosyl complexes $[CoCl_2-(NO)(P(CH_3)(C_6H_5)_2)_2]$, there is no evidence for the existence of an intramolecular redox equilibrium: this would induce a change in the coordination mode of the nitrosyl ligand $NO^+ \rightarrow NO^-$, with consequent changes in central metal oxidation state and geometrical configuration.[6]

Although it was impossible to determine the ^1H nmr spectra for most of the compounds because of their instability in solution, the ^1H nmr spectrum of $[Fe(SCN)(NO)(CO)-(P(CH_3)(C_6H_5)_2)_2]$ in deuterated acetone was found to exhibit an apparent methyl doublet at $\tau \sim 7.6$ ($J(P–H) = 8$ Hz), consistent with two equivalent phosphines.

By employing the bidentate phosphines 1,2-bis(diphenyl-phosphino)ethane (diphos) and *cis*-1,2-diphenylphosphino-ethylene (di=phos) on the $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]^+$ cation it has been possible to substitute both the carbonyl groups and generate the compounds $[Fe(NO)(L-L)(P-(C_6H_5)_3)_2]^+$, where L-L is diphos or di=phos in low yield. Poor analyses were obtained for these cations, and all attempts to purify these crude materials failed.

The ir and nmr data allow us to assign the complexes FeX-(NO)COL$_2$ a trigonal-bipyramidal configuration (I) with a linear Fe–N–O arrangement and the iron atom in the zero formal oxidation state. A trigonal-bipyramidal structure has been assigned by Johnson, *et al.*,[2] for the parent [FeNO-(CO)$_2$L$_2$]$^+$ isoelectronic cation (II) and by Manuel[7] for the isoelectronic Fe(CO)$_3$L$_2$ (III).
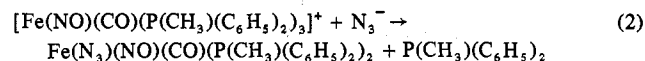
I　　　　　　　　II　　　　　　　III
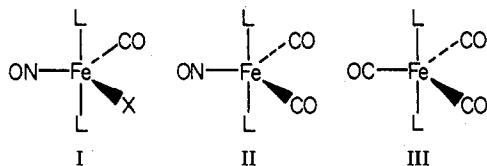
Roper[8] assigned the same geometrical configuration to the ruthenium complexes RuX(NO)(CO)L$_2$ (X = N$_3$, NCO, NCS, OH, I, Br; L = P(C$_6$H$_5$)$_3$). Recent X-ray crystal structure

determinations of the osmium(0) complex[9] $[Os(CO)_2(NO)-(P(C_6H_5)_3)_2]ClO_4 \cdot CH_2Cl_2$ and of the ruthenium(0) complex[10] $[Ru(NO)(diphos)_2]BPh_4 \cdot CH_3COCH_3$ reveal that both species have essentially trigonal-bipyramidal geometries with almost linear M–N–O arrangements located in the plane of the trigonal bipyramid. The Os–N–O angle is $177 \pm 1°$ with the phosphine ligands in trans position, and the Ru–N–O angle is $174°$.

In view of all these results we are inclined to consider the trigonal-bipyramidal geometry as the most appropriate for this type of complex; also in the presence of bulky phosphines it could lead to great distortions.[11]

It is worthwhile to consider briefly the reaction with azide ion which seems to proceed by an unusual pathway. Reactions of metal carbonyls with azide ion generally lead to isocyanato complexes.[12]

Kinetic studies[13] suggest that the first step of the reaction is N_3^- attack with loss of N_2 to form an isocyanato product. The reaction between azide ion and $[Fe(NO)(CO)_2L_2]^+$ (L = P(C$_6$H$_5$)$_3$, P(CH$_3$)(C$_6$H$_5$)$_2$) does not lead to isocyanate derivatives; this is to our knowledge the first reaction involving carbonyl cations which does not follow this path. The complex FeN$_3$(NO)(CO)(P(CH$_3$)(C$_6$H$_5$)$_2$)$_2$ is also formed from the reaction of [Fe(NO)(CO)(P(CH$_3$)-(C$_6$H$_5$)$_2$)$_3$]$^+$ with azide ion

$$[Fe(NO)(CO)(P(CH_3)(C_6H_5)_2)_3]^+ + N_3^- \rightarrow \qquad (2)$$
$$Fe(N_3)(NO)(CO)(P(CH_3)(C_6H_5)_2)_2 + P(CH_3)(C_6H_5)_2$$

The stability of the azide complex and its formation from a

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carbonyl cation is by far the most interesting aspect of these reactions. This unusual result led us to suggest that the latter phenomenon may be due to the presence of the nitrosyl ligand and its stabilization of a six-coordination transition state leading to the ligand substitution, whereas in the other carbonyl cations the azide cannot so readily enter the coordination sphere and hence attacks the carbonyl ligand leading to isocyanate complexes. It is already well known that SN2 type mechanisms are operating in the substitution reactions of nitrosyl complexes.[14]

From ir and nmr data the carbonyl and, in view of the X-ray determinations reported above, the nitrosyl and azide ligands are likely to reside in the equatorial plane in adjacent coordination sites (IV). This is quite unusual. Recently attention was called to a broad class of atom-transfer redox reactions which could be promoted by a metal which held both oxidant and reductant in cis position in the coordination sphere.[15] Thermodynamically favorable processes between kinetically inert reactants might be facilitated by coordination of the potential reactants in adjacent positions.[16] However, in the present case, such reactions do not occur at least at room temperature. Stable d^6 metal complexes have been isolated with carbonyl and azide ligands in cis coordination sites, but we know only two other d^8 metal complexes in which these two potential reactants occupy adjacent coordination sites: $IrN_3(CO)(TDPME)$ (V) (TDPME = 1,1,1-

IV   V
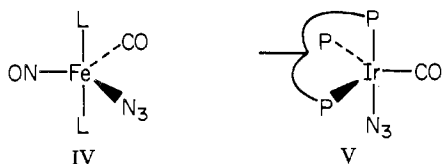
tris(diphenylphosphinomethyl)ethane)[17] and $RuN_3(NO)(CO)(PPh_3)_2$.[8] Among examples of metal ion promoted atom-transfer redox reactions, carbon monoxide is the most common reducing reagent[18] while the isoelectronic NO^+ species can also act as a potential reductant.[19] The presence of these three potential reactants in adjacent positions in the coordination sphere gives rise to possible reactions such as

$$[RuN_3(CO)(NO)(PPh_3)_2] \rightarrow [Ru(N_2)(CO)(PPh_3)_2] + N_2O \quad (3)$$
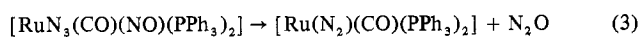
involving combination of adjacent azide and nitrosyl groups, as has been suggested by Roper[8] for ruthenium complexes. Such a reaction, in our case, would lead to an iron–dinitrogen complex. Because the kinetic and thermodynamic stabilities of the iron–dinitrogen complex seem to depend on the presence of hydride ligands,[20] the decomposition of this complex, if it were formed, would not be surprising.

It has long been recognized that both the coordinated

carbonyl[21] and the coordinated nitrosyl[22] groups are readily attacked by bases forming complexes in which the entering base is attached to the carbon or to the nitrogen of the coordinated group.

Johnson and Segal[1,2] reported that methoxide ion attacks at the carbon of the carbonyl group in the cation $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]^+$ to form the carboxy derivative $Fe(NO)(CO)L_2CO_2CH_3$.

In the course of our investigation reactions were carried out between $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]^+$ and a series of primary and secondary amines including monomethylamine, diethylamine, dimethylamine, and isopropylamine with the expectation of some nucleophilic reaction at the coordinated carbonyl group.

Any reaction was expected to occur at the nitrosyl group. The nitrosyl is subject to attack by amines[19b,c] but the carbonyl group seems to be attacked preferentially when both CO and NO are present in the same coordination sphere.[23] No detectable formation of carboxamido complexes $Fe(NO)(CO)(P(C_6H_5)_3)_2$ (CONHR) has been found. In fact only the cationic precursor $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]^+$ could be isolated from the reaction mixture; perhaps an equilibrium situation is involved in the reaction but we did not investigate this possibility. Further studies are being carried out on this question.

Experimental Section

General Information. Microanalyses were performed by Dr. Franz Pascher Laboratorium, Bonn, West Germany.

Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrometer: only selected ir bands have been reported. ^{1}H nmr spectra were measured on a Varian T-60 spectrometer; conductivity measurements were carried out with a LKB 5300 B conductivity bridge. Preparative reactions were carried out under argon, and all solvents were purged with N_2 prior to their use.

Nitrosonium hexafluorophosphate was acquired from Alfa Inorganics, and the starting complexes $[Fe(NO)(CO)_2L_2]PF_6$ were prepared by the published procedure.[1]

The phosphines and the inorganic salts were used as commercial products without further purification.

Preparation of $FeN_3(NO)(CO)L_2$. In a typical preparation 2 g (12.46 mmol) of $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]PF_6$ were suspended in 100 ml of a water solution of 2 g (15.4 mmol) of sodium azide. Acetone was added to a 100-ml maximum, until the iron(0) complex just dissolved and the solution became homogeneous. The reaction mixture was stirred for 5 hr. The red compound that precipitated from the solution was filtered and washed with water, methanol, and finally diethyl ether. The product was dried *in vacuo*; yield 90%.

The other complexes were prepared in a similar way adding the appropriate sodium salt to the $[Fe(NO)(CO)_2L_2]PF_6$ (L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$) complexes.

Analytical data and some physical properties for these complexes are collected in Table I.

Reaction of $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]PF_6$ with Amines. In a typical experiment, the nitrosyl complex (0.200 g) was suspended in diethyl ether and a saturated amine solution was added dropwise. No reaction occurred and the starting compound was recovered unreacted after the solvent evaporation.

Reaction with Bidentate Phosphine. A 0.5-g (0.6-mmol) sample of $[Fe(NO)(CO)_2(P(C_6H_5)_3)_2]^+$ was treated with twice the stoichiometric amount of bidentate phosphine in boiling methanol (80 ml) for 24 hr. After cooling, the reaction mixture was reduced to a small volume. Addition of benzene precipitated a crystalline green compound with a 30% di=phos yield and a brown compound with a

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(23) L. Busetto, G. Dolcetti, A. Palazzi, and D. Pietropaolo, *J. Organometal. Chem.*, in press.

28% di=phos yield. Attempts to purify these crude products further failed to give pure complexes.

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Contribution from the Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

Iron Carbonyl Complexes of Thioureas and Thioamides

HOWARD ALPER* and ALBERT S. K. CHAN

This paper describes the reactions of various thioureas (and several thioamides) with diiron enneacarbonyl. Fully substituted thioureas and thioamides react with $Fe_2(CO)_9$ at room temperature to give sulfur-donor ligand iron tetracarbonyl complexes, diiron hexacarbonyl complexes having both nitrogen and sulfur donor ligands, and the known $S_2Fe_3(CO)_9$. Tetramethylthiourea rather than carbonyl ligand displacement occurred on treatment of tetramethylthioureairon tetracarbonyl with tri-n-butylphosphine. Thioureairon tetracarbonyls and bis(thiourea)iron tricarbonyls, as well as triiron octacarbonyl complexes [and $S_2Fe_3(CO)_9$], were obtained from reactions of disubstituted and trisubstituted thioureas with $Fe_2(CO)_9$. Thiobenzanilide and 5-methyl-3-phenyl-2-thiohydantoin gave similar complexes.

Although the broad area of organosulfur–metal carbonyl complexes has been investigated in considerable detail,[1] few publications have appeared in the literature concerning the reactions of thioureas with metal carbonyls. Treatment of thiourea with rhenium[2] or manganese[3,4] pentacarbonyl chloride, o-phenanthrolinemolybdenum tetracarbonyl,[5] and cycloheptatrienemolybdenum tricarbonyl[6] gives sulfur-donor ligand complexes (*e.g.*, 1). Very recently, Abel and Dunster[7]

$$Re(CO)_5Cl + (NH_2)_2C=S \rightarrow [(NH_2)_2C=S]_2Re(CO)_3Cl + 2CO$$
$$\mathbf{1}$$
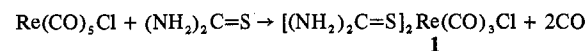
noted that reaction of manganese pentacarbonyl bromide with N,N-dimethyl-N'-phenyl-N'-trimethylstannylthiourea afforded the binuclear manganese carbonyl complex 2.

2
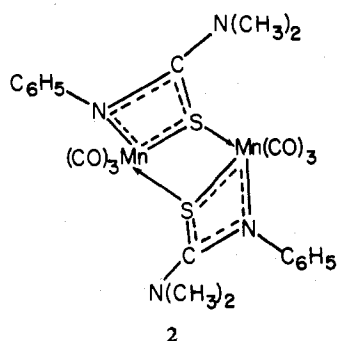
This paper describes, to our knowledge, the first examples of thiourea–iron carbonyl complexes. The purpose of this

study was to determine what type of complexes was formed on reaction of various thioureas with diiron enneacarbonyl (*i.e.*, complexes of type **1**, **2**, or other). In particular, we were interested in learning what effect a hydrogen atom, present on at least one of the nitrogen atoms of the thiourea, had on the course of the reaction. As an aid in assigning structures for the complexes formed in the thiourea–$Fe_2(CO)_9$ reactions, several thioamides were also treated with the enneacarbonyl.

Results and Discussion

The fully alkylated thiourea, tetramethylthiourea (3a), reacts with $Fe_2(CO)_9$ in ether at room temperature to give the highly air-sensitive sulfur-donor ligand complex 4a, the reasonably air-stable diiron hexacarbonyl complex 5a, and 6, a known[8,9] sulfur–iron carbonyl. Complexes analogous

$R = N(CH_3)_2$ (a), CH_3 (b), C_6H_5 (c)
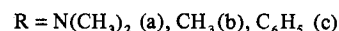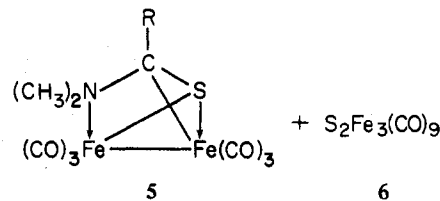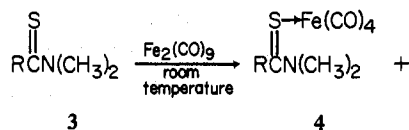
to 4a and 5a (as well as some 6) were isolated from the reactions of the metal carbonyl with N,N-dimethylthioacetamide (3b) and N,N-dimethylthiobenzamide (3c). No sulfur-donor ligand ortho-metalated complex[10] was formed from

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