402. *The Reactions of Carbon Monoxide and Nitric Oxide with Tertiary Phosphine Complexes of Iron*(II), *Cobalt*(II), *and Nickel*(II).

By G. Booth and J. Chatt.

Carbon monoxide reacts under mild conditions with $[FeCl_2(PEt_nPh_{3-n})_2]$ ($n = 0$—3), forming well-defined adducts $[FeCl_2(CO)_2(PEt_nPh_{3-n})_2]$ except where $n = 0$. Complexes $[CoX_2(PEt_nPh_{3-n})_2]$ (X = Cl, Br, or I) form unstable adducts, only these with $n = 3$, *i.e.*, $[CoX_2(CO)(PEt_3)_2]$, being isolable. The corresponding nickel complexes do not form adducts, but the dinitrites and dinitrates, *e.g.*, $[Ni(NO_3)_2(PEt_nPh_{3-n})_2]$, are reduced to nitrosyl nitrites and nitrates, respectively, *e.g.*, $[Ni(NO_3)(NO)(PEt_nPh_{3-n})_2]$, even at room temperature and pressure.

Nitric oxide in similar circumstances yields intractable oils from the iron complexes and a series of diamagnetic unstable adducts $[CoX_2(NO)(PEt_3)_2]$ from $[CoX_2(PEt_3)_2]$. The nickel complexes are oxidised to the known phosphine oxide complexes *e.g.*, $[NiX_2(POEt_3)_2]$ from $[NiX_2(PEt_3)_2]$.

In general, the complexes of the more aliphatic phosphines react more readily and give products more stable than those of the more aromatic precursors.

OUR work [1] on the carbonylation of organo-complexes of the type *trans*-$[MXR(PEt_3)_2]$ (M = Pd or Pt; R = alkyl or aryl; X = Cl, Br, or I), and especially the ready reaction of the palladium complexes with carbon monoxide, led us to study the reactions of carbon monoxide with related halogeno-complexes of other metals under moderate conditions of temperature and pressure.

Previous work in this field involved rather vigorous conditions. For instance, the complex $[CoI_2(PPh_3)_2]$ in the presence of copper and carbon monoxide at 70°/200 atm. gives the salt $[Co(CO)_3(PPh_3)_2][CuI_2]$;[2] and $[ReX_2(PPh_3)_2]$ * under similar conditions but with the addition of triphenylphosphine yields $[ReX(CO)(PPh_3)_2]$, $[ReX(CO)_2(PPh_3)_2]$, or $[ReX(CO)_3(PPh_3)_2]$ depending on the conditions.[3] The nickel complex $[NiBr_2(PPh_3)_2]$ with carbon monoxide alone at 180°/15 atm. gives $[Ni(CO)_3(PPh_3)]$.[4]

We find that even at room temperatures and moderate pressures carbon monoxide reacts with halogeno-transition metal complexes containing tertiary phosphines, especially when the phosphine is aliphatic, and here we report the reactions of carbon monoxide and nitric oxide with complexes of the general type $[MX_2(PEt_nPh_{3-n})]$ (M = Fe, Co, or Ni; X = Cl, Br, I, or NO_3; $n = 0$—3).

Iron Complexes.—Iron complexes of the type $[FeX_2(PR_3)_2]$ are not generally known

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* *Added in proof.* This was incorrectly formulated in ref. 3. It is $[ReO(OEt)X_2(PPh_3)_2]$ (cf. *Chem. and Ind.*, 1962, 40, 92); hence the formulæ of the derived carbonyl complexes are suspect.

[1] Booth and Chatt, *Proc. Chem. Soc.*, 1961, 67.

[2] Sacco and Freni, *J. Inorg. Nuclear Chem.*, 1958, **8**, 566.

[3] Freni and Valenti, *J. Inorg. Nuclear Chem.*, 1961, **16**, 240.

[4] Yamamoto, *Bull. Chem. Soc. Japan*, 1954, **27**, 516.

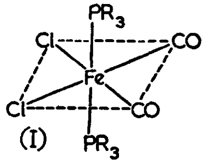
because they dissociate in solution, especially in hydroxylic solvents. For this reason Jensen[5] failed in his attempt to prepare $[FeCl_2(PEt_3)_2]$ in alcoholic solution. Only the triphenylphosphine complexes are known and the chloride is variously described as yellow and colourless.[6,7] We have now prepared all the complexes $[FeCl_2(PEt_nPh_{3-n})_2]$ by dissolving anhydrous ferrous chloride in boiling benzene containing an excess of the tertiary phosphine. The colourless needles of the triethylphosphine complex were too unstable for accurate analysis and the formula is assumed by analogy and on the basis of approximate analysis. The cream ethyldiphenylphosphine complex was the most stable and the colourless triphenylphosphine complex only slightly less stable. The magnetic moments of the stable members of this series indicate that they have four unpaired electrons, *i.e.*, have the " high-spin " tetrahedral configuration rather than the alternative planar configuration with two unpaired electrons.

All the above compounds except the triphenylphosphine complex react with carbon monoxide, to form diamagnetic, yellow-to-brown octahedral carbonyl complexes of the type $[FeCl_2(CO)_2(PR_3)_2]$. Configuration (I) is assigned to them on the basis of their dipole moments and infrared spectra (two very strong sharp carbonyl stretching bands in the 2000 cm.$^{-1}$ region) (Table 1). Significantly, this is the configuration in which the most strongly double-bonding ligands, the carbonyl groups, are in *trans*-positions to the weakly double-bonding halogen atoms. Thus the *d*-orbitals of the metal can make the maximum contribution to double bonding and so to metal-to-ligand bond strength. These octahedral dicarbonyl complexes are moderately stable in air, being generally more stable than the tetrahedral complexes from which they were prepared. In this series of dicarbonyl complexes the triethylphosphine complex is the most stable and the triphenylphosphine complex is by far the least stable.

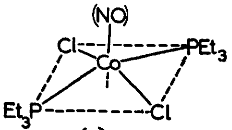
TABLE 1.

Compound	M. p.*	ν(CO) † (cm.$^{-1}$)	Dipole moment (D)
$[FeCl_2(CO)_2(PEt_3)_2]$	106°	2014, 1963	3·95
$[FeBr_2(CO)_2(PEt_3)_2]$	110	2009, 1958	4·1
$[FeI_2(CO)_2(PEt_3)_2]$	96	2003, 1953 ‡	4·2
$[Fe(NCS)_2(CO)_2(PEt_3)_2]$	119	2030, 1983	8·1 §
$[FeCl_2(CO)_2(PEt_2Ph)_2]$	130	2025, 1972	4·1
$[FeCl_2(CO)_2(PEtPh_2)_2]$	160	2033, 1980	4·2

* Determined on a Kofler hot-stage; all compounds decomp., with evolution of gas on melting. † In carbon tetrachloride at 20°. ‡ Spectrum changes with time; see text. § Not diagnostic for configuration; may be (I) or corresponding configuration with Cl replaced by PEt_3 and PR_3 by NCS.



(I)



(II)

The above dicarbonyl complexes were formed readily from the triethylphosphine and diethylphenylphosphine ferrous chloride complexes, by reaction of carbon monoxide at atmospheric temperature and pressure with the benzene solutions in which the starting phosphine complexes were prepared. The ethyldiphenylphosphine ferrous chloride complex did not react at atmospheric pressure but did so readily at 55 atm. On the other hand, the analogue $[FeCl_2(PPh_3)_2]$ did not react with carbon monoxide under pressure at room temperature, and at elevated temperature and pressure it decomposed. Nevertheless the carbonyl $[FeCl_2(CO)_2(PPh_3)_2]$ is the only member of the above series

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[5] Jensen, *Z. anorg. Chem.*, 1936, **229**, 282.
[6] Naldini, *Gazzetta*, 1960, **90**, 391.
[7] Issleib and Döll, *Z. anorg. Chem.*, 1960, **305**, 1.

which had previously been reported. It had been prepared from $[FeCl_2(CO)_4]$,[8] and we have also obtained a rather poor specimen of it from $[Fe(CO)_3(PPh_3)_2]$ and chlorine; its instability hinders purification. The compounds obtained in these reactions are listed in Table 1 together with a bromide, iodide, and thiocyanate which were obtained by metathetical reaction of the appropriate alkali-metal salt with the corresponding chloride. The iodide $[FeI_2(CO)_2(PEt_3)_2]$ is considerably less stable that the corresponding chloride or bromide, and the infrared spectrum of its solution in carbon tetrachloride or hexane changes very rapidly owing to isomerisation or decomposition.

The reaction of nitric oxide with the bis-tertiary-phosphine ferrous chloride complexes gave only oily inseparable mixtures. This is not entirely unexpected since nitric oxide would oxidise any free phosphine to the phosphine oxide. Solutions even of the pure complexes $[FeX_2(PR_3)_2]$ contain free phosphine in dissociation equilibrium, and so oxidation by nitric oxide would lead to complete destruction of the complex. Some nitrosyl complexes were formed, however, since the infrared spectra of the oily products had two strong bands in the 1700—1800 $cm.^{-1}$ region, which might be attributed to NO stretching frequencies.

Cobalt Complexes.—The complexes $[CoX_2(PR_3)_2]$ are much less dissociated than their iron analogues in solution and are prepared in ethanol.[5,9] Reaction of the iodide $[CoI_2(PPh_3)_2]$ with carbon monoxide has already been reported.[2] We have found that other cobalt complexes of this type containing diethylphenylphosphine or ethyldiphenylphosphine also react readily with carbon monoxide and nitric oxide, to give rather intractable products. However, the complexes $[CoX_2(PEt_3)_2]$ ($X = Cl$, Br, and I) give reasonably stable carbonyl complexes and these we have isolated and studied.

The above triethylphosphine complexes in organic solvents rapidly absorb one molecule of carbon monoxide or nitric oxide at room temperature and pressure, with a change of colour from blue or green to dark brown. When the reaction is carried out in benzene the dark brown complexes $[CoX_2(CO)(PEt_3)_2]$, $[CoCl_2(NO)(PEt_3)_2]$, and $[CoBr_2(NO)(PEt_3)_2]$ can readily be isolated. However, the iodide $[CoI_2(PEt_3)_2]$ with nitric oxide gives only an oil and the solid material $[CoI_2(NO)(PEt_3)_2]$ is best prepared from the corresponding chloronitrosyl complex.

The cobalt carbonyl and nitrosyl complexes are much less stable than the corresponding iron dicarbonyl complexes. They decompose on exposure to the atmosphere. Whereas the stability of the cobalt carbonyl complexes increases in passing from the chloride to the iodide, that of the corresponding nitrosyl decreases. The compounds and their properties are listed in Table 2. The mononitrosyl complexes are peculiar in showing two bands in the 1650—1750 $cm.^{-1}$ region where the spectrum is measured at room temperature, but when the chloride is cooled to —70° the higher-frequency band is eliminated. Thus the lower-frequency absorption may be attributed to the normal NO stretching vibration in the complex. The origin of the other band is uncertain; it might be caused by free oxides of nitrogen owing to dissociation of the complex, or perhaps by some equilibrium between different types of bonding of the nitrosyl group. Absorption in the

TABLE 2.

Compound	M. p.*	ν(CO or NO) ($cm.^{-1}$)	Dipole moment (D)	Magnetic moment (B.M.)
$[CoCl_2(CO)(PEt_3)_2]$	58° †	1977 ‡	—	—
$[CoBr_2(CO)(PEt_3)_2]$	84—85	1975 ‡	—	—
$[CoI_2(CO)(PEt_3)_2]$	97—98	1973 ‡	3·0	1·89
$[CoCl_2(NO)(PEt_3)_2]$	79—81	1646 §	1·8	~0
$[CoBr_2(NO)(PEt_3)_2]$	91—92	1731, 1657 §	—	—
$[CoI_2(NO)(PEt_3)_2]$	98	1744, 1690 §	—	—

* In evacuated tube. † With decomp. ‡ In CCl_4 at 20°. § In hexane at —70°.

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[8] Hieber and Thalhofer, *Angew. Chem.*, 1956, **68**, 679.

[9] Chatt and Shaw, *J.*, 1961, 285.

higher-frequency region (1700—1750 cm.$^{-1}$) is also characteristic of the nitrosyl group in the complexes $[NiX(NO)(PEt_nPh_{3-n})_2]$ (see Table 3).

5-Co-ordinated complexes of cobalt(II) are rare and our attempts to obtain a complex $[CoI_2(PEt_3)_3]$ corresponding to the most stable carbonyl complex $[CoI_2(CO)(PEt_3)_2]$ were not successful. However, a substance $[CoBr_2(PHPh_2)_3]$ is known[10] and the formation of such complexes may depend critically upon the organic phosphine. Chatt and Shaw[11] observed similar critical dependence on the phosphine when they prepared the complex $[Ni(C{\equiv}CPh)_2(PEt_2Ph)_3]$ but were unable to obtain analogous complexes from other tertiary phosphines.

The configuration of the 5-co-ordinated carbonyl and nitrosyl cobalt complexes is uncertain. The nitrosyl complex is diamagnetic and therefore is isoelectronic, so far as the cobalt atom is concerned, with the dithiocarbamate complex $[Co(S_2C{\cdot}NMe_2)_2(NO)]$ which has a molecular structure based on the square pyramid with the NO at the apex.[12] The new cobalt nitrosyl complexes probably have a similar stereochemistry as in (II). The *trans*-arrangement of the phosphine and chloro-groups about the metal atom in the chloride (II) accords with its low dipole moment.

Nickel Complexes.—Whereas the iron and cobalt complexes of the type $[MX_2(PEt_3)_2]$ all have tetrahedral configurations, those of nickel are usually planar although some, such as the dinitrate and the triphenylphosphine complexes, are tetrahedral. Both were tested for the formation of simple adducts with carbon monoxide and nitric oxide, but none was isolated. Generally, reaction with carbon monoxide led to reduction in the valency state of the nickel or reduction of the nitrate ligands; reaction with nitric oxide led to the oxidation of the phosphine and the formation of the phosphine oxide complexes.

The halide complexes, *e.g.*, *trans*-$[NiBr_2(PEt_3)_2]$, and the tetrahedral $[NiBr_2(PPh_3)_2]$ in benzene solution do not react with carbon monoxide under moderate conditions, *e.g.*, 50°/2 atm.; and at 70°/75 atm. substituted carbonyls of nickel(0), *e.g.*, $[Ni(CO)_3(PPh_3)]$, are produced. In the aliphatic series these were unstable oils which were not characterised.

The tetrahedral dinitrato-complexes, *e.g.*, $[Ni(NO_3)_2(PEt_3)_2]$, are interesting because at room temperature with carbon monoxide they readily yield nitrato-nitrosyl complexes, *e.g.*, $[Ni(NO_3)(NO)(PEt_3)_2]$. The ease of this reduction strongly suggests that it must be initiated by adduct formation. The corresponding planar *trans*-dinitro-compound underwent similar, but slightly less rapid, reduction to the complex $[Ni(NO_2)(NO)(PEt_3)_2]$, indicating that the reduction of the nitrato-complex does not depend on its having a tetrahedral configuration. The triphenylphosphine dinitrato-complex $[Ni(NO_3)_2(PPh_3)_2]$ reacts rather more sluggishly at 15°/50 atm. of carbon monoxide, giving the corresponding nitrato-nitrosyl complex and under more vigorous conditions (70°/65 atm.) yielded the nickel(0) complex $[Ni(CO)_2(PPh_3)_2]$.

The nitroso-complexes $[NiX(NO)(PR_3)_2]$ (Table 3) obtained by metathetical reactions with the corresponding alkali halide from the above nitrato-nitrosyl complexes are dark brown to violet and often strongly pleochroic, as are the tetrahedral compounds $[NiX_2(PPh_3)_2]$.[13] The complex $[NiBr(NO)(PPh_3)_2]$ is identical with Feltham's bromo-nitrosyl complex obtained from $[NiBr_2(PPh_3)_2]$ and sodium nitrite.[14]

In the above nickel nitrosyl complexes the nitrosyl stretching frequencies are in the range assigned to NO^+ by Lewis, Irving, and Wilkinson.[15] Thus the nickel atom has the same electronic configuration as it has in nickel(0) complexes, and the above nitrosyls would be expected to have a tetrahedral arrangement of ligands. The dipole moments of about 7 D are in agreement with this. The complexes are slightly paramagnetic when

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[10] Issleib and Wenschuh, *Z. anorg. Chem.*, 1960, **305**, 15.
[11] Chatt and Shaw, *J.*, 1960, 1718.
[12] Alderman and Owston, *Nature*, 1956, **178**, 1071.
[13] Venanzi, *J. Inorg. Nuclear Chem.*, 1958, **8**, 137.
[14] Feltham, *J. Inorg. Nuclear Chem.*, 1960, **14**, 307.
[15] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

TABLE 3.

Compound	M. p.*	Colour	ν(NO) (cm.$^{-1}$)	Dipole moment (D)
$[NiCl(NO)(PEt_3)_2]$	53—54°	Dark brown	1706 ‡	—
$[NiBr(NO)(PEt_3)_2]$	74—75	Dark brown	1708 ‡	—
$[NiI(NO)(PEt_3)_2]$	75—77	Dark brown	1723 ‡	7·1
$[Ni(NO_2)(NO)(PEt_3)_2]$	41—42	Dark violet-brown	1705 ‡	7·1
$[Ni(NO_3)(NO)(PEt_3)_2]$	Oil	Violet	1750	—
$[NiBr(NO)(PEtPh_2)_2]$	144—145 †	Blue-brown	1727 §	—
$[NiBr(NO)(PPh_3)_2]$	200—205	Violet	1730 §	6·85
$[NiI(NO)(PPh_3)_2]$	168—170	Blue	1738 §	—

* Determined on a Kofler hot-stage. † With decomp. ‡ In hexane at 20°. § In carbon tetrachloride at 20°.

they are freshly prepared, but in several weeks under nitrogen they become appreciably paramagnetic.

Nitric oxide reacts rapidly with both planar and tetrahedral complexes of nickel(II) and tertiary phosphines, to form the corresponding tertiary phosphine oxide complexes, *e.g.*, $[NiBr_2(OPEt_3)_2]$ and $[Ni(NO_3)_2(OPEt_3)_2]$, identical with the substances prepared by Issleib and Mitscherling directly from the phosphine oxide.[16] These phosphine oxide complexes do not react with carbon monoxide at 1 atm.

EXPERIMENTAL

The carbonyl and nitrosyl complexes were handled in an inert atmosphere. Evaporations were carried out at ~20 mm. M. p.s were determined on a Kofler hot-stage, except those marked * which were determined in evacuated tubes. A representative selection of the carbonyl and nitrosyl complexes was shown to be electrically non-conducting in nitrobenzene. Pressure reactions were carried out in stainless-steel tubes (capacity 100—200 c.c.) in a Baskerville rocking autoclave. Carbon monoxide and nitric oxide were obtained from commercial cylinders.

Iron Complexes.—Dichlorobis(triphenylphosphine)iron(II) $[FeCl_2(PPh_3)_2]$.[6,7] Triphenylphosphine (10·5 g.) and anhydrous ferrous chloride (1·3 g.) were boiled in benzene (60 c.c.) for 6 hr. The mixture was filtered whilst hot, and colourless crystals of dichlorobis(triphenylphosphine)-iron(II) separated on cooling (Found: C, 66·25; H, 4·7; Cl, 11·35. Calc. for $C_{36}H_{30}Cl_2FeP_2$: C, 66·4; H, 4·65; Cl, 10·9%).

Dichlorobis(ethyldiphenylphoshine)iron(II) $[FeCl_2(PEtPh_2)_2]$. Ethyldiphenylphosphine (8 g., 4 mol.) and ferrous chloride (1·2 g.) in benzene (30 c.c.) were heated under reflux for 3 hr. and the hot solution was filtered. The *product* separated on cooling and recrystallised from benzene (40 c.c.) as cream prisms (2·5 g.), m. p.* 185—187° (Found: C, 60·6; H, 5·55; Cl, 12·9%; *M*, ebullioscopically in 0·8% benzene solution, 538. $C_{28}H_{30}Cl_2FeP_2$ requires C, 60·6; H, 5·45; Cl, 12·8%; *M*, 555), $\mu_{eff.}$ 5·1 B.M., dipole moment *ca.* 6·3 D (solution in benzene unstable).

Dichlorobis(diethylphenylphosphine)iron(II) $[FeCl_2(PEt_2Ph)_2]$. Prepared in a similar way from ferrous chloride and diethylphenylphosphine the *complex* was obtained as cream needles, m. p.* 70—73° (Found: C, 52·5; H, 6·6. $C_{20}H_{30}Cl_2FeP_2$ requires C, 52·3; H, 6·6%), $\mu_{eff.}$ 4·7 B.M.

Dichlorodicarbonylbis(triethylphosphine)iron(II) $[FeCl_2(CO)_2(PEt_3)_2]$. Triethylphosphine (9 g., 4 mol.) and ferrous chloride (2·4 g.) in benzene (60 c.c.) were heated under reflux for 3 hr. After cooling and filtration from a little insoluble material, the violet solution (almost colourless when hot) was shaken at 15° under carbon monoxide at atmospheric pressure until absorption of gas ceased (6 days; 550 c.c.). The resulting dark brown solution was evaporated. The residue, recrystallised from acetone (40 c.c.), yielded *dichlorodicarbonylbis(triethylphosphine)-iron*(II) as dark yellow prisms (3 g.) (Found: C, 40·0; H, 7·4; Cl, 16·9%; *M*, ebullioscopically in 0·28% benzene solution, 446; *M*, in 0·85% benzene solution, 410. $C_{14}H_{30}Cl_2FeO_2P_2$ requires C, 40·1; H, 7·2; Cl, 16·9%; *M*, 419).

Dichlorodicarbonylbis(diethylphenylphosphine)iron(II) $[FeCl_2(CO)_2(PEt_2Ph)_2]$ was similarly prepared from diethylphenylphosphine (6·7 g.) and ferrous chloride (1·3 g.) in benzene (30 c.c.) [3 days' absorption of CO (200 c.c.)] as orange prisms (0·35 g.) (Found: C, 51·4; H, 6·0%;

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[16] Issleib and Mitscherling, *Z. anorg. Chem.*, 1960, **304**, 73.

M, ebullioscopically in 0·94% benzene solution, 504. $C_{22}H_{30}Cl_2FeO_2P_2$ requires C, 51·3; H, 5·9%; *M*, 515).

Dichlorodicarbonylbis(ethyldiphenylphosphine)iron(II) $[FeCl_2(CO)_2(PEtPh_2)_2]$. Dichlorobis(ethyldiphenylphosphine)iron (2 g.) in benzene (40 c.c.) was treated for 24 hr. with carbon monoxide at 10°/55 atm. The resulting yellow solution was evaporated and the residue recrystallised, from acetone then from ethyl methyl ketone, to give *dichlorodicarbonylbis(ethyldiphenylphosphine)iron*(II) as yellow prisms (Found: C, 59·4; H, 5·05; Cl, 11·65. $C_{30}H_{30}Cl_2FeO_2P_2$ requires C, 58·95; H, 4·95; Cl, 11·6%).

Metathetical Reactions of Iron Complexes.—Dibromodicarbonylbis(triethylphosphine)iron(II) $[FeBr_2(CO)_2(PEt_3)_2]$. Dichlorodicarbonylbis(triethylphosphine)iron (0·2 g.) in methanol (20 c.c.) was heated under reflux for 2 hr. with potassium bromide (0·2 g.) in water (2 c.c.). The *dibromo-complex* crystallised, on cooling, as bronze plates (0·13 g.) which were recrystallised from methanol (Found: C, 33·4; H, 5·95. $C_{14}H_{30}Br_2FeO_2P_2$ requires C, 33·1; H, 5·95%).

Di-iododicarbonylbis(triethylphosphine)iron(II) $[FeI_2(CO)_2(PEt_3)_2]$. The dichloro-complex (0·4 g.) in methanol (30 c.c.) was heated under reflux for 1 hr. with potassium iodide (0·4 g.) in water (4 c.c.). The *di-iodo-complex* crystallised on cooling, as brown needles (0·13 g.) which were recrystallised from methanol (Found: C, 27·9; H, 5·05%; *M*, ebullioscopically in 1·256% benzene solution, 594. $C_{14}H_{30}FeI_2O_2P_2$ requires C, 27·9; H, 5·0%; *M*, 602).

Di(isothiocyanato)dicarbonylbis(triethylphosphine)iron(II) $[Fe(NCS)_2(CO)_2(PEt_3)_2]$. The dichloro-complex (0·4 g.) in methanol (30 c.c.) was heated under reflux for 1 hr. with potassium thiocyanate (0·4 g.) in water (4 c.c.). The *di(isothiocyanato)-complex* crystallised, after partial evaporation of the solution, as yellow needles (Found: C, 41·0; H, 6·6; N, 5·75. $C_{16}H_{30}FeN_2O_2P_2S_2$ requires C, 41·4; H, 6·5; N, 6·0%). This compound is designated an isothiocyanate on the basis of a strong band at 824 cm.$^{-1}$ (Nujol mull).[17]

Cobalt Complexes.—The tertiary phosphine-cobalt halide complexes were prepared by established methods.[5,9]

Di-iodo(carbonyl)bis(triethylphosphine)cobalt(II) $[CoI_2(CO)(PEt_3)_2]$. A green solution of di-iodobis(triethylphosphine)cobalt (0·5 g.) (Found: C, 26·4; H, 5·5. $C_{12}H_{30}CoI_2P_2$ requires C, 26·25; H, 5·5%) in benzene (25 c.c.) was shaken for 20 min. under carbon monoxide at 15°/1 atm. It became dark brown after 20 c.c. (*ca.* 1 mol.) of carbon monoxide had been absorbed. The solution was evaporated and the residue recrystallised several times from light petroleum (b. p. 30—40°) with cooling to −10°, to give *di-iodo(carbonyl)bis(triethylphosphine)cobalt*(II) as dark brown prisms (Found: C, 27·2; H, 5·25%; *M*, cryoscopically in 0·97% benzene solution, 543. $C_{13}H_{30}CoI_2OP_2$ requires C, 27·1; H, 5·2%; *M*, 577).

Analogously dibromobis(triethylphosphine)cobalt and dichlorobis(triethylphosphine)cobalt with carbon monoxide gave, respectively, *dibromo(carbonyl)bis(triethylphosphine)cobalt*(II) as dark brown plates (Found: C, 32·2; H, 6·3; Br, 33·2. $C_{13}H_{30}Br_2CoOP_2$ requires C, 32·3; H, 6·3; Br, 33·1%), and *dichloro(carbonyl)bis(triethylphosphine)cobalt*(II) as dark brown prisms (Found: C, 39·75; H, 8·2; Cl, 18·2. $C_{13}H_{30}Cl_2CoOP_2$ requires C, 39·6; H, 7·7; Cl, 18·0%).

Dichloro(nitrosyl)bis(triethylphosphine)cobalt(II) $[CoCl_2(NO)(PEt_3)_2]$. Nitric oxide was bubbled through a blue solution of dichlorobis(triethylphosphine)cobalt (1 g.) in benzene (100 c.c.) for 10 min. The solution became dark brown within 4 min. and was evaporated, after decantation from an insoluble oil. The residue, recrystallised several times from light petroleum (b. p. 40—60°), with cooling to −10°, gave *dichloro(nitrosyl)bis(triethylphosphine)cobalt*(II) as dark brown needles (Found: C, 36·35; H, 7·9; Cl, 17·5; N, 3·4%; *M*, cryoscopically in 0·59% benzene solution, 386. $C_{12}H_{30}Cl_2CoNOP_2$ requires C, 36·4; H, 7·65; Cl, 17·9; N, 3·5%; *M*, 396).

Dibromo(nitrosyl)bis(triethylphosphine)cobalt(II), $[CoBr_2(NO)(PEt_3)_2]$, was prepared analogously from dibromobis(triethylphosphine)cobalt as dark brown needles from light petroleum (b. p. 40—60°) (Found: C, 29·3; H, 6·5; N, 2·8. $C_{12}H_{30}Br_2CoNOP_2$ requires C, 29·7; H, 6·25; N, 2·9%).

Di-iodo(nitrosyl)bis(triethylphosphine)cobalt(II) $[CoI_2(NO)(PEt_3)_2]$, Dichloro(nitrosyl)bis(triethylphosphine)cobalt (0·14 g.) in acetone (10 c.c.) was treated with potassium iodide (0·14 g.) in water (1·5 c.c.). The resultant mixture was evaporated and the residue recrystallised from light petroleum (b. p. 30—40°), with cooling to −10°, to give *di-iodo(nitrosyl)bis(triethylphosphine)cobalt*(II) as dark brown needles (0·1 g.) (Found: C, 25·15; H, 5·4; N, 2·4. $C_{12}H_{30}CoI_2NOP_2$ requires C, 24·9; H, 5·2; N, 2·4%).

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[17] Turco and Pecile, *Nature*, 1961, **191**, 66.

Nickel Complexes.—(*A*) *Preparation.* Complexes of the type $[NiX_2(PR_3)_2]$ (X = Cl, Br, NO_2, or NO_3; R = alkyl or aryl) were prepared by established methods.[18,19]

In an analogous way were prepared *dinitratobis(diethylphenylphosphine)nickel*(II), green plates, m. p. 100—105° (from ethanol) (Found: C, 46·35; H, 6·0; N, 5·2. $C_{20}H_{30}N_2NiO_6P_2$ requires C, 46·6; H, 5·9; N, 5·45%), *dinitratobis(ethyldiphenylphosphine)nickel*(II), green prisms, m. p. 155—175° (from ethanol) (Found: C, 54·7; H, 4·85. $C_{28}H_{30}N_2NiO_6P_2$ requires C, 55·0; H, 4·95%), and trans-*dinitrobis(triethylphosphine)nickel*(II), orange needles, m. p. 163—169° (decomp.) (from methanol) (Found: C, 37·5; H, 7·9. $C_{12}H_{30}N_2NiO_4P_2$ requires C, 37·25; H, 7·8%). The last compound is designated " dinitro " on the basis of bands at 1370vs, 1318vs, and 821s $cm.^{-1}$.[20]

(*B*) *Action of carbon monoxide on nickel complexes.* (1) Dibromobis(triphenylphosphine)-nickel (1 g.) in benzene (40 c.c.) was heated for 7 hr. with carbon monoxide at 60—70°/60 atm. The resultant mixture was filtered from a small quantity of orange solid, and the solution was evaporated. By two recrystallisations from light petroleum (b. p. 40—60°), the residue gave tricarbonyl(triphenylphosphine)nickel(0) (0·11 g.) as colourless prisms, m. p.* 120° (decomp.) (Found: C, 62·15; H, 3·75. Calc. for $C_{21}H_{15}NiO_3P$: C, 62·25; H, 3·75%). Its infrared spectrum was identical with that of an authentic specimen.[21]

(2) *trans*-Dinitrobis(triethylphosphine)nickel (1 g.) in benzene (50 c.c.) was treated for 15 min. with carbon monoxide at 15°/1 atm. The resultant violet-brown solution was evaporated and the residue twice recrystallised from light petroleum (b. p. 40—60°), to give *nitronitrosylbis(triethylphosphine)nickel* (0·34 g.) as needles (Found: C, 38·45; H, 8·35; N, 7·55%; *M*, ebullioscopically in 0·5% benzene solution, 364. $C_{12}H_{30}N_2NiO_3P_2$ requires C, 38·8; H, 8·15; N, 7·55%; *M*, 371).

(3) Dinitratobis(triethylphosphine)nickel (1 g.) in benzene (40 c.c.), similarly, with carbon monoxide gave a residue of crude nitratonitrosylbis(triethylphosphine)nickel as a violet oil. This oil, when dissolved in water (75 c.c.) and treated with an aqueous solution of potassium iodide (1 g.), yielded a blue-grey precipitate which recrystallised from light petroleum (b. p. 30—40°) to give *iodonitrosylbis(triethylphosphine)nickel* (0·3 g.) as needles (Found: C, 32·05; H, 6·9; N, 2·9%; *M*, ebullioscopically in 1% benzene solution, 442. $C_{12}H_{30}INNiOP_2$ requires C, 31·9; H, 6·7; N, 3·1%; *M*, 452). Similarly an aqueous solution of crude nitratonitrosylbis(triethylphosphine)nickel with potassium chloride, potassium bromide, or sodium nitrite yielded precipitates which on recrystallisation from light petroleum (b. p. 40—60°) gave, respectively, *chloro-* (needles) (Found: C, 39·9; H, 8·3. $C_{12}H_{30}ClNNiOP_2$ requires C, 40·0; H, 8·4%), *bromo-* (needles) (Found: C, 35·75; H, 7·5; N, 3·35. $C_{12}H_{30}BrNNiOP_2$ requires C, 35·6; H, 7·5; N, 3·45%), and nitro-nitrosylbis(triethylphosphine)nickel (needles) (Found: C, 38·95; H, 8·15%).

(4) Dinitratobis(ethyldiphenylphosphine)nickel (1 g.) in benzene (80 c.c.) was treated for 20 min. with carbon monoxide at 15°/1 atm. The resultant green solution became violet overnight and was then evaporated. The violet, glassy residue was dissolved in ethanol (50 c.c.) and lithium bromide (1 g.) in ethanol (20 c.c.) was added. Evaporation then yielded *bromonitrosylbis(ethyldiphenylphosphine)nickel* as blue prisms. These recrystallised from ethanol as brown prisms (0·15 g.) (Found: C, 56·6; H, 5·5. $C_{28}H_{30}BrNNiOP_2$ requires C, 56·3; H, 5·05%).

(5) Dinitratobis(triphenylphosphine)nickel (1 g.), suspended in benzene (40 c.c.), was treated for 24 hr. with carbon monoxide at 15°/50 atm. Unchanged dinitrato-complex was filtered off and the resultant grey-blue solution evaporated. The blue oily residue [crude nitratonitrosylbis(triphenylphosphine)nickel] in ethanol (20 c.c.) was treated with an ethanolic solution of sodium iodide (1 g.), and evaporated, giving *iodonitrosylbis(triphenylphosphine)nickel* as brown prisms. These recrystallised from ethanol as blue plates (Found: C, 58·0; H, 4·5; N, 1·75. $C_{36}H_{30}INNiOP_2$ requires C, 58·4; H, 4·1; N, 1·9%). Similarly the crude nitrato-complex, on treatment with lithium bromide, gave bromonitrosylbis(triphenylphosphine)-nickel[14] (Found: C, 62·7; H, 4·65; N, 2·2. Calc. for $C_{36}H_{30}BrNNiOP_2$: C, 62·4; H, 4·35; N, 2·0%).

Dinitratobis(triphenylphosphine)nickel (0·8 g.) in benzene (20 c.c.) was heated for 7 hr. with carbon monoxide at 70°/65 atm. The resultant solution was filtered and evaporated. The

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[18] Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.
[19] Venanzi, *J.*, 1958, 719.
[20] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.
[21] Chatt and Hart, *J.*, 1960, 1378.

residue, recrystallised twice from light petroleum (b. p. 40—60°), yielded dicarbonylbis(triphenylphosphine)nickel(0) as cream prisms, m. p.* 210° (decomp.), of which the infrared spectrum was identical with that of an authentic specimen.[21]

(*C*) *Action of nitric oxide on nickel complexes.* (1) *trans*-Dibromobis(triethylphosphine)nickel (1 g.) in benzene (25 c.c.) was treated for 15 min. with nitric oxide at 15°/1 atm. The resultant dark green solution, decanted from a small quantity of oil, was evaporated; the green-blue residue, recrystallised twice from toluene, yielded dibromobis(triethylphosphine oxide)nickel[16] (0·3 g.) as bright blue prisms, m. p. 93° (Found: C, 30·1; H, 6·15. Calc. for $C_{12}H_{30}Br_2NiO_2P_2$: C, 29·6; H, 6·2%).

TABLE 4.

Dipole moments.

	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_{T}P$	$_{E}P$	$_{O}P$	μ (D)
$[FeCl_2(CO)_2(PEt_3)_2]$ ……	1·754	4·362						
	2·418	4·378						
	37·61		6·72					
	40·84		6·16					
	9·263			0·389				
	10·54			0·370	440·9	108·9	315·7	3·95
$[FeBr_2(CO)_2(PEt_3)_2]$ ……	3·842	3·872	—	—	—			
	5·055	3·848	—	(0·46)	473 *	(115)	342 *	4·1 *
$[FeI_2(CO)_2(PEt_3)_2]$ ………	2·058	3·365						
	2·595	3·428						
	25·56		2·75					
	26·30		2·85					
	4·976			0·543				
	7·161			0·543	493·2	115·0	360·9	4·20
$[Fe(NCS)_2(CO)_2(PEt_3)_2]$…	1·372	15·90	—	—				
	1·701	15·88	—	(0·46)	1485 *	(124)	1343 *	8·1 *
$[FeCl_2(CO)_2(PEt_2Ph)_2]$ …	3·333	3·970	—					
	3·912	4·042	—	(0·38)	507 *	(139)	347 *	4·1 *
$[FeCl_2(CO)_2(PEtPh_2)_2]$ …	1·421	3·641	—	—	—			
	1·634	3·556	—	(0·38)	554 *	(168)	360 *	4·2 *
$[CoI_2(CO)(PEt_3)_2]$ ………	1·989	1·826	—					
	2·001	1·890	—	(0·45)	321 *	(122)	181 *	3·0 *
$[CoCl_2(NO)(PEt_3)_2]$ ……	5·033	1·439	—					
	5·964	1·438	—	(0·45)	189·5 *	(107·4)	66·0 *	1·8 *
$[Ni(NO_2)_2(PEt_3)_2]$ ………	5·474	0·985	—					
	6·432	0·987	—	(0·32)	167·2 *	(105·6)	45·8 *	1·5 *
$[Ni(NO_2)(NO)(PEt_3)_2]$ …	3·44	15·01	—					
	4·164	15·37	—	(0·38)	1147 *	(98)	1034 *	7·1 *
$[NiI(NO)(PEt_3)_2$ ………	2·502	12·42	—					
	3·494	12·15	—	(0·38)	1149 *	(104)	1029 *	7·1 *
$[NiBr(NO)(PPh_3)_2]$ ……	3·511	7·799	—					
	3·657	7·762	—	(0·38)	1174 *	(188)	958 *	6·85 *

(2) Dinitratobis(triethylphosphine)nickel (1 g.) in benzene (40 c.c.) was treated for 15 min. with nitric oxide at 15°/1 atm. Light petroleum (b. p. 40—60°; 20 c.c.) was added to the resultant yellow solution; the precipitated yellow prisms recrystallised from benzene to give dinitratobis(triethylphosphine oxide)nickel[16] (0·5 g.), m. p. 86—96° (Found: C, 31·8; H, 7·0; N, 5·95. Calc. for $C_{12}H_{30}N_2NiO_8P_2$: C, 31·95; H, 6·7; N, 6·2%).

Physical Measurements.—The detailed results for dipole moments are shown in Table 4, the method of determination and the notation being as previously described.[22] Errors are about ±0·2 D for moments less than 3·5 D, and about ±0·1 D for moments greater than 3·5 D. Asterisks denote that the values of $_{T}P$, $_{O}P$, and μ were calculated by using the values of $-\Delta v/w$ and $_{E}P$ (in parentheses) which were estimated (see ref. 22).

Infrared spectra were measured on a Grubb–Parsons GS2A spectrometer.

Microanalyses are by the Microanalytical Department of these laboratories.

Magnetic moments were measured by the Faraday method.[23]

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[22] Chatt and Shaw, *J.*, 1959, 705.

[23] Blaha, *Mikrochem. Mikrochim. Acta*, 1952, **39**, 339.