Inorganic Grignard Analogues. Reaction of Nickel Powder with Dihalogenotriorganophosphorus Compounds to form Nickel-(II) and -(III) Phosphine Complexes; Isolation of Planar $[Ni(PPh_3)I_3]^-$ and the Crystal Structure of $[Ni(PPhMe_2)_2Br_2]$†

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Reactions of dihalogenotriorganophosphorus compounds R_3PX_2 (X = Br or I) with unactivated coarse-grain nickel metal powder have been investigated. The nature of the nickel phosphine complexes formed is remarkably dependent on both R and X. Where R ≠ Me and X = I the nickel(II) complexes $[R_3PI][Ni(PR_3)I_3]$ are formed, analogous to, but not isostructural with, similar cobalt complexes of the same stoichiometry formed from cobalt powder and R_3PI_2. Quantitative electronic spectroscopic studies indicated that, surprisingly, the $[R_3PI][Ni(PR_3)I_3]$ complexes all have predominantly square-planar geometry around nickel. Where R = Me and X = I, the nickel(III) complex $[Ni(PMe_3)_2I_3]$ is obtained in quantitative yield, the other product being diiodine. Reaction of nickel powder with Me_2PhPI_2 yields both the nickel(II) complex, $[Me_2PhPI][Ni(PPhMe_2)I_3]$, and the nickel(III) complex, $[Ni(PPhMe_2)_2I_3]$. These observations again mirror analogous cobalt reactions. Reaction of the analogous dibromo compounds, R_3PBr_2, with nickel powder is extremely sensitive to the nature of R. Where R = Me, Et or Pr^n no reaction occurs; where $R_3 = PhMe_2$ the square-planar complex $[Ni(PPhMe_2)_2Br_2]$ and an octahedral complex of stoichiometry $Ni(PPhMe_2)_2Br_4$ are obtained in equal yield. Where $R_3 = Ph_2Pr^n$ the octahedral complex $[Ni(PPh_2Pr^n)_2Br_4]$ is formed with a trace of the planar complex $[Ni(PPh_2Pr^n)_2Br_2]$, and where R = Ph the octahedral complex $[Ni(PPh_3)_2Br_4]$ is formed in quantitative yield. The complex $[Ni(PPhMe_2)_2Br_2]$ has been crystallographically characterised: monoclinic, space group $P2_1/a$, $a = 10.018(2)$, $b = 10.249(1)$, $c = 10.138(1)$ Å and $Z = 2$ (molecule centrosymmetric).

Nickel(II) complexes of tertiary phosphines have been widely studied.[1,2] The commonest complex formed is the bis species $[Ni(PR_3)_2X_2]$; where R_3 = triaryl the complexes are usually monomeric and tetrahedral,[3] for R_3 = trialkyl or aryldialkyl square-planar complexes[4] are formed, but for R_3 = alkyldiaryl there frequently results a tetrahedral–planar isomerism.[5] With trimethylphosphine a good deal of variation exists, and $[Ni(PMe_3)_2X_2]$, $[Ni(PMe_3)_3X_2]$, $[Ni(PMe_3)_4X]X$ and $[Ni(PMe_3)_5]X_2$ (X = Cl, Br, I, NCS or CN) have all been observed.[6,7] The four-co-ordinate complexes are all *trans*-planar, and the five-co-ordinate are trigonal bipyramidal (with, where appropriate, axial halides). The equilibrium nature of the interaction of NiX_2 with PMe_3 has been studied in detail.[7]

In addition to the more familiar nickel(II) complexes, the unstable nickel(III) species, $[Ni(PR_3)_2X_3]$, have received some attention. The first of these were synthesised in 1936 by Jensen,[8] and reinvestigated by the same worker in 1963;[9] it was concluded that these complexes are trigonal bipyramidal with axial phosphines. However, it was not until recently that a comprehensive study of the $[Ni(PR_3)_2X_3]$ complexes (R_3 = Me_3, Et_3, $Bu^n{}_3$, $PhMe_2$, $PhEt_2$ or Ph_2Me; X = Cl or Br) was reported by Levason and co-workers,[10] who synthesised these complexes by oxidation of the respective $[Ni(PR_3)_2X_2]$ with NOX at low temperatures. The complexes were shown by visible spectroscopy, magnetic and nickel-edge extended X-ray absorption fine structure (EXAFS) data to be monomeric trigonal-bipyramidal species with axial phosphines, in agreement with the earlier conclusions of Jensen *et al.*[8,9] Prior to our work only one such complex, $[Ni(PMe_3)_2I_3]$, had been crystallographically characterised. This compound, obtained serendipitously from the reaction of $[\{Ni(\mu\text{-}Bu^t{}_2As)(PMe_3)_2\}_2]$ with diiodine,[11] was shown to be distorted trigonal bipyramidal with axial phosphines; the distortion was rationalised on the basis of Jahn–Teller effects in a $3d^7$ system. There has also been an X-ray diffraction study of the interesting mixed-oxidation-state (+2, +3) species $2[Ni(PPhMe_2)_2Br_3]\cdot[Ni(PPhMe_2)_2Br_2]\cdot2C_6H_6$ of Stalick and Ibers,[12] with the nickel(III) fragment again being trigonal bipyramidal.

We report here studies of the production of nickel-(II) and -(III) complexes by a novel route. Conventional synthesis of transition-metal phosphine complexes usually involves a reaction of type (1). Our synthesis employs *unactivated* metal powders [equation (2)]. This synthetic method can lead to the

$$MX_2 + nPR_3 \longrightarrow [M(PR_3)_nX_2] \qquad (1)$$

$$M + nX_2PR_3 \longrightarrow [M(PR_3)_nX_x] \qquad (2)$$

production of known metal complexes *e.g.* $[Mn(PPh_3)_2I_2]$[13] and $[Ni(PPhMe_2)_2Br_2]$ (present work), complexes in high oxidation states *e.g.* $[Fe(PPhMe_2)_2Br_3]$, $[Ni(PMe_3)_2I_3]$[14] and $Co(PMe_3)_2I_3]$,[15] dinuclear complexes with mixed oxidation states *e.g.* $[Mn_2(PMe_3)_3I_5]\cdot PMe_3$,[16] complexes of novel isomers *e.g.* $[Mn(PPhMe_2)I_2]$,[14] complexes of unusual stoichiometry *e.g.* $[Zn(PEt_3)I_2]$[17] and 'frozen transition state' species *e.g.* $\{[Bu^n{}_3PI]_2(\mu\text{-}I)][Bu^nPI](\mu\text{-}I)CoI_3\}$.[15] It is thus apodictic that this unexpected activation of coarse-grain metal powers by dihalogenotriorganophosphoranes can expand the existing boundaries of metal–phosphine co-ordination chemistry. The systems are, in a way, reminiscent of the Grignard complexes, *cf.* P–X + M ⟶ P–M–X and C–X + Mg ⟶ C–Mg–X.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and spectroscopic data for the iodo-complexes

Complex	Analysis (%)[a] C	H	I	$^{31}P-\{^1H\}$ NMR[b] (δ)	$\tilde{\nu}$(P–I)/cm^{-1}
$[Ph_3PI][Ni(PPh_3)I_3]$	39.3 (39.6)	2.6 (2.7)	46.6 (46.6)	43.4, −9.7	160
$[(PhCH_2CH_2)_3PI][Ni\{P(CH_2CH_2Ph)_3\}I_3]$	46.9 (45.7)	4.6 (4.3)	39.1 (40.3)	77.4, 37.4, −5.9	163
$[Me_2PhPI][Ni(PPhMe_2)I_3]$	23.0 (22.8)	2.7 (2.6)	59.8 (60.3)	53.3, 5.0	204
$[Bu^n{}_3PI][Ni(PBu^n{}_3)I_3]$	29.3 (29.7)	5.5 (5.6)	53.5 (52.3)	98.3, −94.3	197
$[Et_3PI][Ni(PEt_3)I_3]$	16.8 (17.9)	3.4 (3.7)	63.3 (63.5)	—	232
$[MeEt_2PI][Ni(PEt_2Me)I_3]$	15.8 (15.5)	3.5 (3.4)	65.1 (65.5)	—	209
$[(Me_2N)_3PI][Ni\{P(NMe_2)_3\}I_3]$[c]	15.6 (16.1)	3.9 (4.0)	58.6 (56.9)	—	225
$[Ni(PPhMe_2)_2I_3]$	27.1 (26.8)	3.2 (3.1)	52.9 (53.2)	—	—
$[Ni(PMe_3)_2I_3]$	12.5 (12.2)	3.1 (3.0)	63.9 (64.4)	—	—

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$ solution relative to concentrated phosphoric acid standard. [c] N 8.6 (9.4)%.

Table 2 Electronic spectral bands for the complexes in 1,2-dichloroethene

Complex	Colour	λ/nm (ε/dm^3 mol^{-1} cm^{-1})		
$[Ph_3PI][Ni(PPh_3)I_3]$	Red		562.01 (405.5)	746.5
$[(PhCH_2CH_2)_3PI][Ni\{P(CH_2CH_2Ph)_3\}I_3]$	Red		525.5 (399.7)	724.5
$[Bu^n{}_3PI][Ni(PBu^n{}_3)I_3]$	Red		524.5 (390.8)	723.0
$[Et_3PI][Ni(PEt_3)I_3]$	Red		523.0 (424.3)	720.0
$[MeEt_2PI][Ni(PEt_2Me)I_3]$	Red		523.5 (415.7)	720.5
$[Ni(PPhMe)_2I_3]$	Black	445 (sh)	541.0 (> 6000)[a]	740
$[Ni(PMe_3)_2I_3]$	Black	390 (sh)	525.7 (8910)	727.2
$[Ph_3PBr][Ni(PPh_3)Br_3]$	Pale blue	402.8	—	646.4 (6.02)
$[Pr^nPh_2PBr][Ni(PPh_2Pr^n)Br_3]$	Pale blue	494.0	601 (sh)	649.0 (3.93)
$[Me_2PhPBr][Ni(PPhMe_2)Br_3]$	Blue	493.6	603 (sh)	649.4 (3.90)
$[Ni(PPhMe_2)_2Br_2]$	Red		509.3 (401)	
$[Ni(PPh_2Pr^n)_2Br_2]$[b]	Pale red		519.0	

[a] Approximate value, see text. [b] Not isolated, see text.

Results and Discussion

The Ionic Complexes $[R_3PI][Ni(PR_3)I_3]$.—These species, Table 1, were synthesised from the addition of 2 equivalents of R_3PI_2 to coarse-grain unactivated nickel powder in dry diethyl ether [equation (3)]; R_3 = $MeEt_2$, Et_3, $Bu^n{}_3$, $(NMe_2)_3$,

$$2R_3PI_2 + Ni \xrightarrow[Et_2O]{60\,^{\circ}C,\ 7d,\ N_2} [R_3PI][Ni(PR_3)I_3] \qquad (3)$$
$$(100\%)$$

$(CH_2CH_2Ph)_3$, $PhMe_2$ or Ph_3]. Visible spectral bands of the complexes are contained in Table 2, and are indicative of square-planar geometry for the $[Ni(PR_3)I_3]^-$ anion. This is a most surprising result for the case of $[Ni(PPh_3)I_3]^-$, as this composition of ligands is expected to enforce a tetrahedral geometry about the metal atom.[18] It has previously been shown[3] that $[Ni(PPh_3)_2X_2]$ (X = Cl, Br or I) have a tetrahedral geometry, and that $[NiX_2(PPh_2R)_2]$ (R = alkyl) frequently exhibit planar–tetrahedral isomerism;[5] indeed $[Ni\{PPh_2(CH_2Ph)\}_2Br_2]$ crystallises as a mixture of both geometries.[19]

Although anions of the type $[Ni(PR_3)X_3]^-$ are rare, they are not unknown, and crystal structures of $[Ph_4As][Ni(PPh_3)I_3]$[18] and $[Bu^t{}_4N][Ni(PBu^t{}_3)Br_3]$,[20] prepared by conventional synthetic methods, reveal tetrahedral geometry about nickel. The visible spectrum of $[Bu_4N][Ni(PPh_3)I_3]$ exhibits bands at '< 600' and 765 nm, the latter being assigned to the $^3T_{1g}(F) \longrightarrow {}^3A_{2g}$ transition for a tetrahedral nickel centre.[3]

The visible spectrum of the complex $[Ph_3PI][Ni(PPh_3)I_3]$, listed in Table 2, is illustrated in Fig. 1. For all the complexes of this formula a major d–d transition at *ca.* 530 nm is observed (with minor bands in the 600–800 nm region which might be attributable to a tetrahedral centre). Clearly, the complexes exist predominantly as the square-planar species although some equilibration is observed in solution. Absorption coefficients ε = 391–424 dm^3 mol^{-1} cm^{-1}, Table 2, were again consistent with planar nickel(II) complexes. Finally, the diamagnetic or slightly paramagnetic susceptibility properties confirm the planar geometry of the $[Ni(PR_3)I_3]^-$ moieties. This slight paramagnetism made the $^{31}P-\{^1H\}$ NMR spectra slightly noisy but, nonetheless, interpretable; resonances obtained are contained in Table 1. In the spectrum of each compound a peak directly assignable to $[R_3PI]^+$ is observed, the assignment of which can be made with confidence by comparison with our solution studies on analogous $[R_3PI]I$ species.[21] In addition,

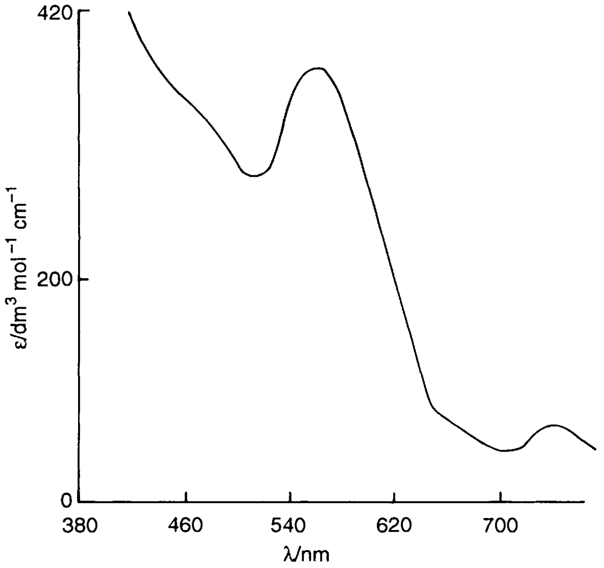

Fig. 1 Visible spectrum of $[Ph_3PI][Ni(PPh_3)I_3]$

each spectrum exhibits one or more additional major resonances, which may be presumably assigned to the phosphorus atom contained in the $[Ni(PR_3)I_3]^-$ anion. Where $R_3 = Et_3$ or Et_2Me the complexes decomposed too rapidly to enable consistent results to be recorded, however. In contrast to these spectra, attempts to obtain a $^{31}P\text{-}\{^1H\}$ NMR spectrum of the nickel(III) complex $[Ni(PMe_3)_2I_3]$ (see below) resulted in only an extremely broad peak covering the entire spectrum, additional evidence, albeit indirect, of the diamagnetism of the $[R_3PI][Ni(PR_3)I_3]$ complexes.

Further evidence regarding our assignment of the $[R_3PI][Ni(PR_3)I_3]$ formulation is provided by the low-frequency Raman spectra. Each spectrum clearly exhibits a strong band assignable to ν(P–I); this band occurs almost at the same frequency as those of the $[R_3PI][Co(PR_3)I_3]$ complexes, for which there is X-ray crystallographic evidence for an ionic structure.[22] The low-frequency Raman spectrum of $[(PhCH_2CH_2)_3PI][NiP(PhCH_2CH_2)_3I_3]$ is illustrated in Fig. 2 and compared to that of the parent diiodotriorganosphosphorus compound $(PhCH_2CH_2)_3PI_2$; both exhibit a ν(P–I) absorption at almost the same frequency.

Attempts to obtain crystals of these nickel complexes were unsuccessful because of instability in a range of organic solvents. Nevertheless, assignment of a planar structure to the anion in $[Ph_3PI][Ni(PPh_3)I_3]$ on the evidence presented above contrasted so vividly with the crystallographically characterised $[Ph_4As][Ni(PPh_3)I_3]$[18] and $[Ph_3PI][Co(PPh_3)I_3]$,[22] both of which contain the metal in a tetrahedral configuration, that we obtained X-ray powder patterns of $[Ph_3PI][Ni(PPh_3)I_3]$ and $[Ph_3PI][Co(PPh_3)I_3]$, Fig. 3. As can be seen, the patterns are clearly different, confirming the non-tetrahedral geometry of the $[Ni(PPh_3)I_3]^-$ anion. This result once again demonstrates that the synthesis of metal complexes from metal powders and our R_3PX_2 reagents gives unexpected, indeed unpredictable, products.

$[Ni(PMe_3)_2I_3]$.—The reaction of 2 equivalents of Me_3PI_2 with nickel powder at room temperature (r.t.) proceeds according to equation (4). Equation (4) is balanced by the

$$2Me_3PI_2 + Ni \xrightarrow[Et_2O]{r.t.,\ N_2,\ 5\ d} [Ni(PMe_3)_2I_3] + \tfrac{1}{2}I_2 \quad (4)$$

production of 0.5 equivalent of diiodine, and this was quantitatively detected spectrophotometrically. Analytical data are contained in Table 1. The structure[11] of $[Ni(PMe_3)_2I_3]$ is shown schematically in Fig. 4. It is trigonal bipyramidal with equatorial iodines and is isostructural with $[Co(PMe_3)_2I_3]$, and has previously been produced by an adventitious route, *viz.* the reaction of $[\{Ni(\mu\text{-}Bu^t_2As)(PMe_3)_2\}_2]$ with diiodine.[11]

Although nickel(III) complexes of stoichiometry $[Ni(PR_3)_2X_3]$ have been known[8] since 1936, they are rare, and all previous workers have pointed to their instability, especially in solution. This has prevented their characterisation by single-crystal X-ray analysis. Levason's[10] series of complexes $[Ni(PR_3)_2X_3]$ (X = Cl or Br) were stable in the order $PMe_3 \approx PEt_3 > PPhMe_2 \approx PBu^n_3 > PPhEt_2 \geqslant PPh_2Me$, and the triphenylphosphine complexes could not be isolated; the bromo derivatives were more stable than their chloro analogues. All the complexes are reported to decompose after 3–4 d, even when stored in an inert atmosphere at 20 °C; the lifetimes in solution were even shorter, some decomposing after only a few minutes. In contrast, $[Ni(PMe_3)_2I_3]$ is relatively stable, decomposing only after *ca.* 6 h in moist air at room temperature and appearing to be indefinitely stable when stored in an inert atmosphere at room temperature. This is probably due to the stronger binding of the soft Me_3P ligands to the relatively softer NiI_3 moiety (as compared to $NiCl_3$ and $NiBr_3$).

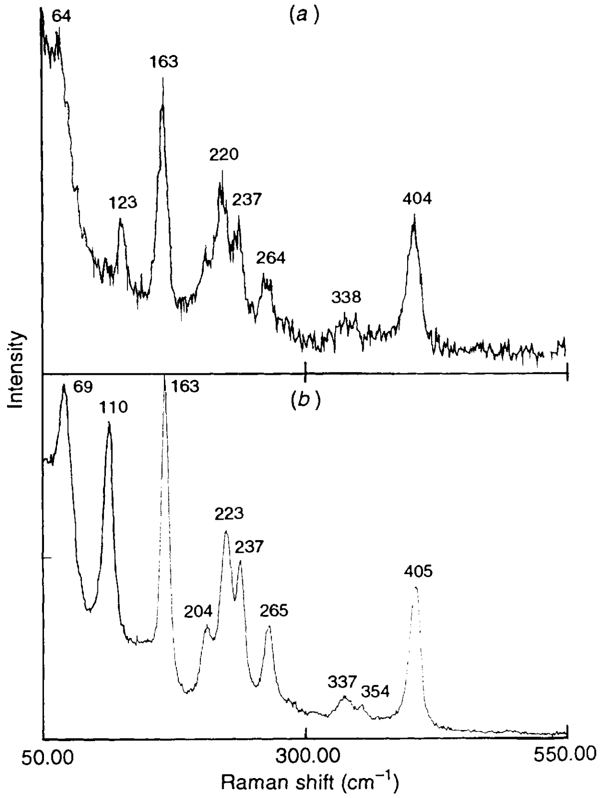

Fig. 2 Comparison of the low-frequency Raman spectra of (*a*) $[(PhCH_2CH_2)_3PI][Ni\{P(CH_2CH_2Ph)_3\}I_3]$ and (*b*) $(PhCH_2CH_2)_3PI_2$

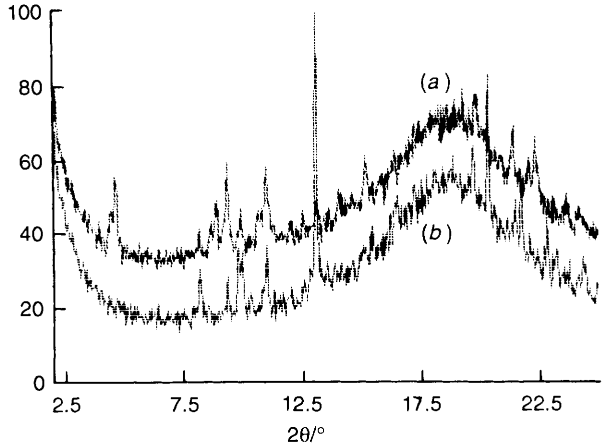

Fig. 3 Comparison of the X-ray powder diffraction patterns of (*a*) tetrahedral $[Ph_3PI][Co(PPh_3)I_3]$ and (*b*) square-planar $[Ph_3PI][Ni(PPh_3)I_3]$

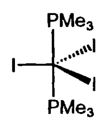

Fig. 4 Schematic representation of the molecular trigonal-bipyramidal complex $[Ni(PMe_3)_2I_3]$

Venanzi and Norgett[23] devised a one-electron transition scheme for the d^7 trigonal-bipyramidal cobalt(II) system, however the assignment of the bands of the nickel(III) complexes at 727 and 526 nm as d–d bands has been questioned by Levason and co-workers[24] since they have very high absorption coefficients and other weaker bands were observed in the near infrared which were assigned to d–d transitions. Consequently, the two bands at 526 and 727 nm in the spectrum of $[Ni(PMe_3)_2I_3]$ are probably due to $P(\sigma) \longrightarrow Ni(a_1)$ and $P(\sigma) \longrightarrow Ni(e_a{}^1)$ transitions respectively, shown in Fig. 5, and there is a shoulder at 390 nm. The two main bands are probably

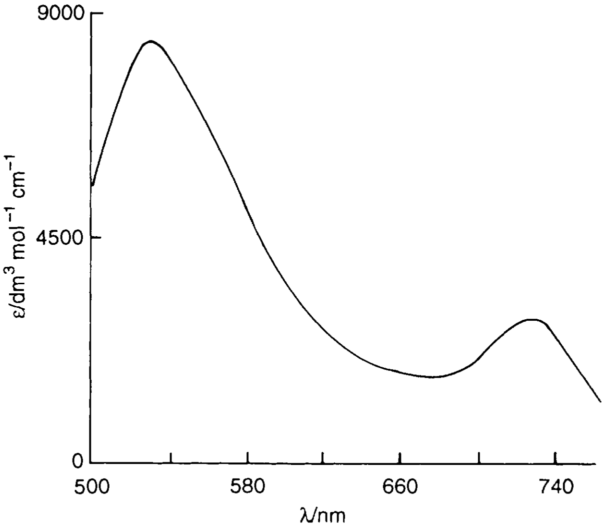

Fig. 5 Visible spectrum of $[Ni(PMe_3)_2I_3]$

the transitions to the $(e'')^4(e')^2(a_1)^1$ and $(e'')^3(e')^3(a_1)^0$ states, respectively, and the broad peak disappearing into the UV region is probably due to ligand-to-metal charge transfer.

Reaction of Me_2PhPI_2 *with Nickel Powder*.—With remarkable analogy to the cobalt system, the reaction of 2 equivalents of Me_2PhPI_2 with nickel powder produces both $[Me_2PhPI][Ni(PPhMe_2)I_3]$ and $[Ni(PPhMe_2)_2I_3]$ in approximately equal yields. Reaction in dry diethyl ether at room temperature over 9 d produces a pale red solid and an intensely purple-black solution. Isolation by Schlenk techniques of the pale red solid $[Me_2PhPI][Ni(PPhMe_2)I_3]$, Table 1, ν(P–I) 204 cm^{-1}, left a dark filtrate. Reduction in volume by vacuum methods and storage at 0 °C for 2 d yielded purple-black crystals, $[Ni(PPhMe_2)_2I_3]$ (Table 1); the electronic spectrum of which exhibits absorptions at 740 and 541 nm, together with a shoulder at 445 nm. The instability of the complex prevented accurate determination of its absorption coefficient; however, an approximate determination indicated a value in excess of 6000 dm^3 mol^{-1} cm^{-1}, evidence for a nickel(III) complex and in reasonable agreement with the value of 8910 dm^3 mol^{-1} cm^{-1}, accurately determined for $[Ni(PMe_3)_2I_3]$ (Table 2). In addition, the value is markedly different from those calculated for the other nickel complexes described herein.

Although cobalt metal also produces $[Me_2PhPI][Co(PPhMe_2)I_3]$ and $[Co(PPhMe_2)_2I_3]$ in an analogous reaction, we note one significant difference between $[Me_2PhPI][Co(PPhMe_2)I_3]$ and $[Me_2PhPI][Ni(PPhMe_2)I_3]$. Whilst a stable electronic spectrum of the cobalt complex is readily obtainable in solution, in diethyl ether the nickel complex slowly darkens and a spectrum identical in profile to $[Ni(PPhMe_2)_2I_3]$ is obtained, evidence for reaction (5) in solution. This apparent

$$[Me_2PhPI][Ni(PPhMe_2)I_3] \longrightarrow [Ni(PPhMe_2)_2I_3] + \tfrac{1}{2}I_2 \quad (5)$$

autoxidation of a nickel(II) to a nickel(III) derivative is most remarkable. Air was excluded from the spectrophotometric cell, and usually the attainment of the III oxidation state is not easy. We are, of course, most interested in the mechanism of the reaction of R_3PX_2 species with metal powders and have, for example, isolated 'frozen transition state' complexes[15] on the way to a metal complex. We also recognise the overwhelming evidence that the R_3PX_2 compounds are ionic $[R_3PX]X$ in solution. Evidence is thus pointing to the $[R_3PX]^+$ species as the active oxidant, as implied by reaction (5).

Reaction of R_3PBr_2 *with Nickel Powder*.—This system is both interesting and puzzling. Two mole equivalents of a large number of R_3PBr_2 (R_3 = Me_3, Et_3, $Pr^n{}_3$, $PhMe_2$, Ph_2Pr^n or Ph_3) were treated with nickel powder in dry diethyl ether in sealed tubes. Surprisingly, where R_3 = Me_3, Et_3 or $Pr^n{}_3$, no reaction was observed even after several months at 60 °C. Careful separation of the white powders from the nickel metal and colourless solvent revealed them to be unreacted R_3PBr_2.

However, the reaction with Me_2PhPBr_2 slowly (5–6 weeks) produces a blue solid and a blood-red liquid. The blue solid has the stoichiometry $Ni(PPhMe_2)_2Br_4$, Table 3. The low-frequency Raman spectrum exhibits a strong band at 249 cm^{-1} which, by comparison with that of Me_2PhPBr_2, Fig. 6, is assignable to ν(P–Br) and, on this basis, the complex is identified as $[Me_2PhPBr][Ni(PPhMe_2)Br_3]$. Dissolving the blue powder in dichloromethane results in the formation of a pale blue solution, the absorption coefficient, 6.02 dm^3 mol^{-1} cm^{-1}, Table 2, being strongly suggestive of an octahedral nickel(II) complex.

The blood-red liquid from the reaction, after careful concentration, yielded dark red crystals after standing for 3 d. This complex, $[Ni(PPhMe_2)_2Br_2]$, Table 2, exhibits a d–d transition in its electronic spectrum at 509 nm (ε_{max} = 401 dm^3 mol^{-1} cm^{-1}) and an intense charge-transfer band centred at 413 nm. The energy and absorption coefficient of the band at 509 nm are typical for the crystallographically characterised square-planar nickel(II) complexes $[Ni(PMe_3)_2Br_2]$, $[Ni(PEt_3)_2Br_2]$, $[Ni\{PPh_2(CH_2Ph)\}_2Br_2]$ and bis(5*H*-dibenzophosphole)dibromonickel.[1]

A crystal of $[Ni(PPhMe_2)_2Br_2]$ was subjected to X-ray analysis, and its structure is shown in Fig. 7; selected bond lengths and angles and fractional atomic coordinates are in Tables 4 and 5 respectively. As expected, the complex adopts a *trans*-planar geometry, well recognised for such complexes containing phosphines of low steric requirement. We can therefore postulate a reaction (6), which is not balanced,

$$4Me_2PhPBr_2 + 2Ni \longrightarrow [Me_2PhPBr][Ni(PPhMe_2)Br_3] + [Ni(PPhMe_2)_2Br_2] \quad (6)$$

however. Both compounds are isolated in approximately equal yield, and there was no evidence for the presence of other products. We must, therefore, conclude that the reaction is more complex than appears from these results.

The range of reactivity is further illustrated in the case of $Pr^nPh_2PBr_2$. When 2 mole equivalents are treated with nickel powder in dry diethyl ether a blue compound $[Pr^nPh_2PBr][Ni(PPh_2Pr^n)Br_3]$, ν(P–Br) 244 cm^{-1}, ε = 3.93 dm^3 mol^{-1} cm^{-1} (electronic spectrum), was obtained in 90–95% yield. However, the filtrate was pale red and, although it was not possible to isolate a solid from this solution its electronic spectrum exhibited a d–d transition centred at 519 nm (and a charge-transfer band at 427 nm), suggesting that the red colour is due to the presence of planar $[Ni(PPh_2Pr^n)_2Br_2]$.

On the other hand reaction of 2 equivalents of Ph_3PBr_2 with nickel gives quantitative yields of the ionic $[Ph_3PBr][Ni(PPh_3)Br_3]$, ν(P–Br) 239 cm^{-1}, ε = 3.90 dm^3 mol^{-1} cm^{-1}, and there is no evidence for the bis(phosphine) planar species. A proposed structure for the complexes $[R_3PBr][Ni(PR_3)Br_3]$ is illustrated in Fig. 8.

Conclusion

These results clearly indicate that the reaction of R_3PX_2 (X = Br or I) with coarse-grain nickel powder in a 2:1 ratio leads to the isolation of a number of products, the nature of which depends crucially on the nature of R and X.

For R_3PI_2 ($R_3 \neq Me_3$ or $PhMe_2$), reaction yields only $[R_3PI][Ni(PR_3)I_3]$; for Me_3PI_2 the only product is the nickel(III) complex $[Ni(PMe_3)_2I_3]$ and for Me_2PhPI_2 two

Table 3 Analytical and spectroscopic data for the bromo-complexes

	Analysis (%)*			
Complex	C	H	Br	$\tilde{\nu}$(P–Br)/cm^{-1}
[Ph_3PBr][$Ni(PPh_3)Br_3$]	47.7 (47.8)	3.1 (3.3)	34.3 (35.4)	237
[Pr^nPh_2PBr][$Ni(PPh_2Pr^n)Br_3$]	41.5 (42.1)	3.7 (4.1)	35.2 (37.3)	244
[Me_2PhPBr][$Ni(PPhMe_2)Br_3$]	29.3 (29.3)	3.6 (3.4)	51.9 (48.8)	249
[$Ni(PPhMe_2)_2Br_2$]	38.8 (38.8)	4.7 (4.4)	31.9 (32.3)	—

* Calculated values in parentheses.

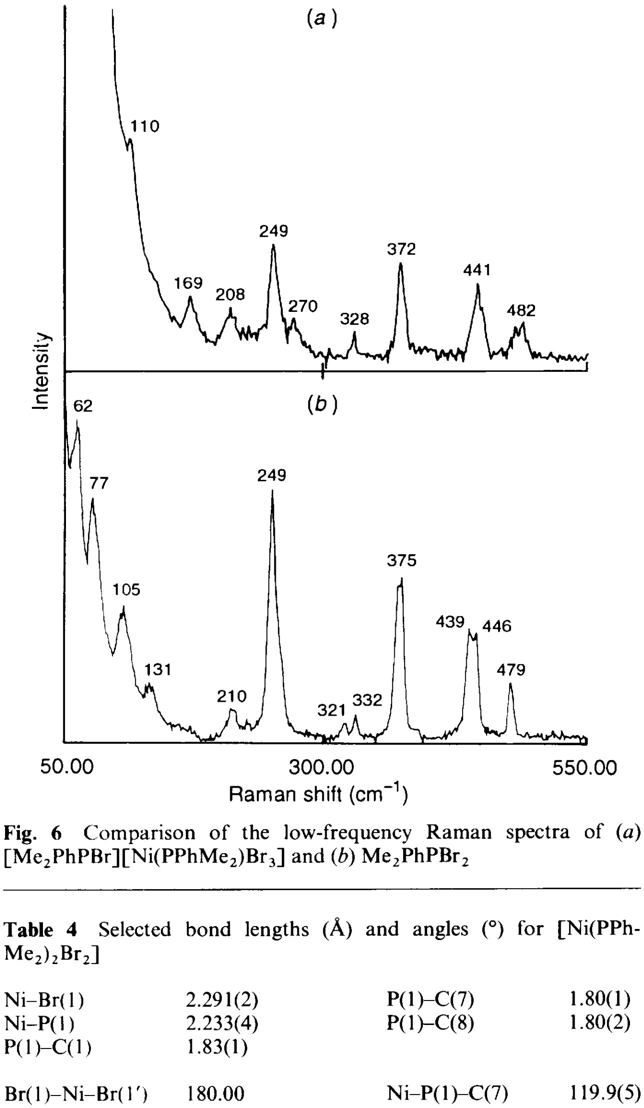

Fig. 6 Comparison of the low-frequency Raman spectra of (*a*) [Me_2PhPBr][$Ni(PPhMe_2)Br_3$] and (*b*) Me_2PhPBr_2

Table 4 Selected bond lengths (Å) and angles (°) for [$Ni(PPhMe_2)_2Br_2$]

Ni–Br(1)	2.291(2)	P(1)–C(7)	1.80(1)
Ni–P(1)	2.233(4)	P(1)–C(8)	1.80(2)
P(1)–C(1)	1.83(1)		
Br(1)–Ni–Br(1′)	180.00	Ni–P(1)–C(7)	119.9(5)
Br(1)–Ni–P(1)	88.1(1)	Ni–P(1)–C(8)	116.5(5)
Br(1)–Ni–P(1′)	91.9(1)	C(1)–P(1)–C(7)	101.6(6)
P(1)–Ni–P(1′)	180.00	C(7)–P(1)–C(8)	100.3(8)
Ni–P(1)–C(1)	108.9(5)		

Primed atoms at $1 - x, 1 - y, 1 - z$.

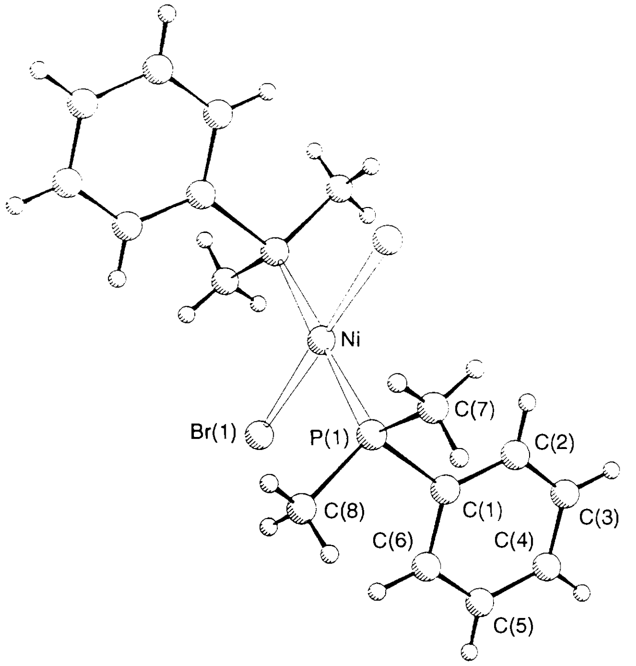

Fig. 7 Crystal structure of *trans*-[$Ni(PPhMe_2)_2Br_2$]

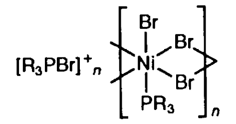

Fig. 8 Schematic representation of the proposed polymeric ionic structure [R_3PBr][$Ni(PR_3)Br_3$]

Table 5 Fractional atomic coordinates for the non-hydrogen atoms in [$Ni(PPhMe_2)_2Br_2$]

Atom	*x*	*y*	*z*
Ni	½	½	½
Br(1)	0.3871(2)	0.3235(1)	0.3662(2)
P(1)	0.3888(5)	0.4527(3)	0.6482(4)
C(1)	0.470(2)	0.306(1)	0.749(2)
C(2)	0.607(2)	0.309(1)	0.852(2)
C(3)	0.667(2)	0.202(2)	0.928(2)
C(4)	0.588(3)	0.088(2)	0.900(2)
C(5)	0.454(2)	0.078(1)	0.796(2)
C(6)	0.390(2)	0.186(1)	0.719(2)
C(7)	0.399(2)	0.564(1)	0.788(2)
C(8)	0.197(2)	0.428(1)	0.569(2)

products are formed in equal amounts, [Me_2PhPI][$Ni(PPhMe_2)I_3$] and [$Ni(PPhMe_2)_2I_3$]. This is superficially an exact mirror of the analogous cobalt system. However, there are some important differences: the [R_3PI][$Co(PR_3)I_3$] complexes contain tetrahedral anions, whereas, surprisingly, the nickel complexes contain square-planar anions, despite the fact that this necessarily involves unfavourable steric interactions. Since [Ph_4As][$Ni(PPh_3)I_3$] has previously been shown by X-ray crystallography to contain a tetrahedral anion,[9] the isolation of a planar isomer here must arise from our method of synthesis, and these results must, necessarily, lead us perhaps to question previous postulations about the relationship between steric requirements of the ligands in, and the resulting structures of, nickel(II) complexes of type [$Ni(PR_3)_2X_2$].

As with cobalt, reaction of nickel with Me_3PI_2 yields a metal(III) complex, [$Ni(PMe_3)_2I_3$]. Nickel(III) compounds are notoriously unstable and have not been at all well studied. A

Table 6 Crystal data and details of refinement for the complex $[NiBr_2(PPhMe_2)_2]$

Formula	$C_{16}H_{22}Br_2NiP_2$
M	494.81
Crystal dimensions/mm	0.2 × 0.2 × 0.2
Colour	Dark red
Crystal system	Monoclinic
Space group	$P2_1/a$ (no. 14)
a/Å	10.018(2)
b/Å	10.249(1)
c/Å	10.138(1)
β/°	111.91(1)
U/Å^3	965.8(5)
Z	2 (molecule centrosymmetric)
D_c/g cm^{-3}	1.701
$F(000)$	492
μ(Mo-Kα)/cm^{-1}	52.63
Total data measured (θ_{max} = 25°)	1915
Transmission factors	0.87–1.13
No. of unique reflections	1807
No. of observed reflections [$I > 4.00\sigma(I)$]	785
No. of parameters	97
Minimum, maximum electron density/e Å^{-3}	−0.86, 0.62
Maximum least-squares shift to error ratio	< 0.01
p in weighting scheme $4F_o^2/\sigma^2(F_o^2)$ for downweighting intense reflections	0.03
Final R	0.061
Final R'*	0.069

* $[\{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}]^{\frac{1}{2}}$.

feature of $[Ni(PMe_3)_2I_3]$ is its relative stability; it should also be mentioned that this complex is produced in a simple one-step synthesis which requires no additional oxidising agent.

Whereas reaction of Me_2PhPI_2 with cobalt and nickel gives a mixture of $[Me_2PhPI][M(PPhMe_2)I_3]$ and $[M(PPhMe_2)_2I_3]$, in the case of nickel (but not cobalt) the $[Me_2PhPI][Ni(PPhMe_2)I_3]$ undergoes a transformation in solution to produce $[Ni(PPhMe_2)_2I_3]$.

The reactions involving R_3PBr_2 are most interesting. These species do not, apparently, react with cobalt metal.[22] Indeed for R_3PBr_2 (R = Me, Et or Pr^n) no reaction is seen for nickel, either. However, for R_3 = $PhMe_2$, Ph_2Pr^n or Ph_3, reaction does occur, but the products vary in a subtle way. Thus, for Me_2PhPBr_2, $[Me_2PhPBr][Ni(PPhMe_2)Br_3]$ and $[Ni(PPhMe_2)_2Br_2]$ are produced in approximately equal amounts, whereas for $Pr^nPh_2PBr_2$ the ionic product is the major product and only a trace of $[Ni(PPh_2Pr^n)_2Br_2]$ is formed; for Ph_3PBr_2 only $[Ph_3PBr][Ni(PPh_3)Br_3]$ is formed.

Experimental

All the nickel complexes described here are moisture sensitive, particularly the nickel(III) complexes, therefore strictly anaerobic and anhydrous conditions were adhered to during their synthesis. The synthesis of the R_3PI_2 compounds has been described elsewhere[21] and the R_3PBr_2 were prepared in an analogous manner. Diethyl ether was obtained commercially (BDH), dried over sodium wire for *ca.* 1 d and then distilled over CaH_2 in an inert atmosphere prior to use. The diethyl ether was then distilled into the reaction vessel and degassed with a nitrogen sparge. Standard reagent-grade coarse-grain nickel powder was obtained from BDH and used as received. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glovebox. The same reaction technique was employed in the synthesis of all the complexes described here in order to establish a reactivity pattern. The synthesis of $[Ni(PMe_3)_2I_3]$ is typical. The compound Me_3PI_2 (1.035 g, 3.136 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) in a rotoflow tube and subsequently nickel powder (0.092 g, 1.568 mmol) was added. After *ca.* 5 d of stirring, the resulting magenta solid was isolated by standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules which were subsequently flame sealed.

Elemental analyses (Table 1) were performed by the analytical laboratory of this department. Electronic spectra were recorded on a Varian Cary 610, a Cecil 6000 or a Shimadzu UV-2101PC spectrophotometer. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5W argon-ion laser and SPEX 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station (NMR spectra). X-Ray powder patterns were recorded on a Scintag XRD2000 powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range 2–25°.

Single-crystal X-Ray Determination.—Suitable crystals of $[Ni(PPhMe_2)_2Br_2]$ were sealed under argon in thin-walled glass capillaries. Cell dimensions and intensity data were recorded as previously described using a Rigaku AFC6S diffractometer.[25] Lorentz, polarisation and absorption (DIFABS)[26] corrections were applied. The structure was solved by direct methods (SHELX 86)[27] and refined by full-matrix least squares (TEXSAN).[28] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealised positions (C–H 0.95 Å) and were assigned equivalent β values 20% greater than the atoms to which they were bonded. Crystal data and experimental details are given in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Mr. P. J. Kobryn (University of Manchester) for recording the Raman spectra, and the SERC for a research studentship (to S. M. G.).

References

1 C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979.

2 W. Levason, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1990, ch. 15, p. 595.

3 F. A. Cotton, O. D. Faust and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1960, **83**, 344; M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 1962, 693; G. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625; J. A. J. Jarvis, R. H. B. Mais and P. G. Owston, *J. Chem. Soc. A*, 1968, 1473.

4 G. Giacometti and A. Turco, *J. Inorg. Nucl. Chem.*, 1960, **15**, 242; L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A*, 1966, 1462; D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, 1976, 1803; K. Shobatake and K. Nakamoto, *J. Am. Chem. Soc.*, 1970, **92**, 3332; B. Corain, B. Longato, R. Angeletti and G. Valle, *Inorg. Chim. Acta*, 1985, **104**, 15.

5 R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 1965, **4**, 1701; L. H. Pignolet and W. DeW. Horrocks, *J. Am. Chem. Soc.*, 1969, **91**, 3977; L. H. Pignolet, W. DeW. Horrocks and R. H. Holm, *J. Am. Chem. Soc.*, 1970, **92**, 1855; G. N. La Mar and E. O. Sherman, *J. Am. Chem. Soc.*, 1970, **92**, 2691; J. T. Wang, C. Udovich, K. Nakamoto, A. Quattrochi and J. R. Ferraro, *Inorg. Chem.*, 1970, **9**, 2675; L. Que and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.

6 M. Dartiguenave, Y. Dartiguenave, A. Gleizes, C. Saint-Jolly, J. Galy, P. Meier and A. E. Merbach, *Inorg. Chem.*, 1978, **17**, 3503; P. F. Meier, A. E. Merbach, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chim. Acta*, 1980, **39**, 19; A. Gleizes, A. Kerkeni, M.

Dartiguenave, Y. Dartiguenave and H. F. Klein, *Inorg. Chem.*, 1981, **20**, 2372.

7 P. F. Meier, A. E. Merbach, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chem.*, 1979, **18**, 610.

8 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 275.

9 K. A. Jensen, B. Nygaard and C. T. Pedersen, *Acta Chem. Scand.*, 1963, **17**, 1126.

10 S. J. Higgins, W. Levason and D. J. Wilkes, *Inorg. Chim. Acta*, 1984, **84**, 1.

11 D. J. Chandler, R. A. Jones and B. R. Whittlesey, *J. Coord. Chem.*, 1987, **16**, 19.

12 J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 453.

13 S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 371.

14 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1447.

15 C. A. McAuliffe, S. M. Godfrey, A. G. Mackie and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 919.

16 C. A. McAuliffe, S. M. Godfrey, A. G. Mackie and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 483.

17 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 944.

18 R. P. Taylor, D. H. Templeton, A. Zalkin and W. DeW. Horrocks, *Inorg. Chem.*, 1968, **7**, 2629.

19 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988, p. 751.

20 E. C. Alyea, A. Costin, G. Ferguson, G. T. Fey, R. G. Goel and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1975, 1294.

21 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.

22 S. M. Godfrey, H. P. Lane, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 1599.

23 L. M. Venanzi and M. J. Norgett, *Inorg. Chim. Acta*, 1968, **2**, 107.

24 J. M. Corker, J. Evans, W. Levason, M. Spicer and P. Andrews, *Inorg. Chem.*, 1991, **30**, 331.

25 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.

26 J. Walker and A. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

27 G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, pp. 175–189.

28 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.

Received 22nd March 1993; *Paper* 3/01626I