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A Comparison of the Donor Properties of some Heterocyclic and Ortho-Substituted Acyclic Triarylphosphines towards Nickel(II) Bromide. The Importance of Steric Effects

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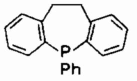
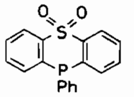
The study of complexes of the type L_2NiX_2 formed between monodentate tertiary phosphines and nickel(II) halides continues to attract interest [1–7]. In this letter, we wish to draw attention to the wide variation in donor properties towards nickel(II) bromide of a series of *ortho*-substituted triarylphosphine ligands, some of which involve the *ortho* substituent as a bridging unit between two aryl rings.

In 1971, we reported that the seven-membered ring cyclic phosphine (1) forms a series of square planar complexes with nickel(II) halides, which were apparently the first recorded square planar nickel(II) halide complexes formed by a triarylphosphine donor [8]. We now find that the six-membered cyclic phosphine (2) similarly forms a diamagnetic nickel(II) bromide complex of the type $(phos)_2NiBr_2$, which by comparison of its solid state diffuse reflectance spectrum with that of the analogous complex of (1) (Table) can also be assigned a square planar geometry.



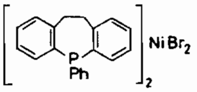
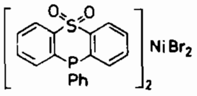
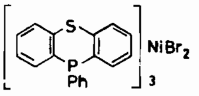
(1)



(2)

Tolman has recently drawn attention to the importance of the steric bulk of ligands in the series $R_3P < R_2PPh < PPh_3$ in increasing the tendency to form tetrahedral nickel(II) halide complexes [9]. It was also suggested that as the size of the phosphine ligands in a tetrahedral complex increases, steric interactions between the phosphine ligands lead to a reopening of the P–Ni–P angle to favour the square planar isomer. In support of this, it was noted that the nickel(II) chloride complex of tricyclohexylphosphine (which has a much larger minimum cone angle than triphenylphosphine) has a square planar structure [10]. However, as this ligand is essentially a trialkylphosphine, it can also be argued [6] that electronic factors are favouring the square planar form. The above *triaryl*phosphines (1) and (2), in contrast, provide unequivocal support for Tolman's thesis, since electronic factors would be assumed to favour the tetrahedral isomer. Molecular models show that these two ligands are both more bulky than triphenylphosphine, as a result of the *o*-bridging groups. Models of the square planar nickel(II) complexes show that in the *trans* square planar configuration, the atoms of the bridging $-CH_2CH_2-$ or SO_2 groups are occupying positions above and below the square planar metal site.

TABLE. Diffuse Reflectance Data for Phosphine–Nickel(II) Bromide Complexes.

Complex	*Colour*	*Absorption Bands ($\bar{\nu}$, cm^{-1})*
	red-brown	23,800; 16,800
	dark brown	23,800; 17,300
$[Ph_2P(o\text{-}ClC_6H_4)]_2NiBr_2$	dull green	23,450; 16,700; 11,100 (weak)
$[Ph_2P(o\text{-}MeOC_6H_4)]_2NiBr_2$	emerald green	23,450; 17,400; 10,800
$(Ph_3P)_2NiBr_2$	green	22,700; 16,650; 10,850
	olive green	21,350; 15,400; 10,650 (weak)

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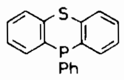
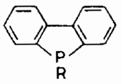
In marked contrast to the cyclic phosphine-sulphone (2), the related phosphine-thioether (3) when added to a solution of nickel(II) bromide in acetic acid in a 2:1 mol ratio forms a diamagnetic, olive green complex of composition $(phos)_3NiBr_2$. The diffuse reflectance spectrum (see Table) whilst similar to those of the above square planar complexes, also shows an additional weak band at 10,650 cm^{-1}. This complex appears to be similar to other complexes of this composition formed by the 5-alkyldibenzophospholes (4, R = Me, Et), which are known to involve 5 coordinate nickel(II) [11].



(3)



(4)

We have also briefly investigated the nickel(II) bromide complexes of diphenyl(*o*-methoxyphenyl)phosphine and *o*-chlorophenyldiphenylphosphine.

Diphenyl(*o*-methoxyphenyl)phosphine forms an emerald green complex of the type $(phos)_2NiBr_2$, having a magnetic moment of 3.6 B.M. and a diffuse reflectance spectrum, by comparison with that of the triphenylphosphine complex, consistent with tetrahedral coordination (Table). Clearly, coordination would seem only to involve the phosphorus atom, as has also been found for platinum(II) complexes of this ligand, in contrast to those of ruthenium(II) where both oxygen and phosphorus are coordinated to the metal [12]. Involvement of the ether oxygen with the metal in square planar iridium(I) complexes of *o*-methoxyphenyldimethylphosphine has also been noted [13]. In contrast, *o*-chlorophenyldiphenylphosphine forms a dull green, diamagnetic complex, of composition $(phos)_2NiBr_2$, whose diffuse reflectance spectrum closely resembles those of the above square planar nickel(II) bromide complexes, except for the appearance of a very weak band at 11,100 cm^{-1}, similar to that observed in the supposedly five coordinate complex of (3). However, the positions of the two major absorption bands in the spectrum of the *o*-chlorophenyldiphenylphosphine complex correlate much more closely with those present in the spectra of the square planar complexes than with those of the five coordinate complex. Possibly, the greater bulk of the *o*-chlorosubstituent compared to the *o*-oxygen atom of the methoxyphenyl ligand favours the square planar form.

Clearly, further studies of the coordination behaviour of the above ligands are desirable in order to fully resolve the factors governing the types of complex formed, but it is apparent that steric factors have a much greater effect in determining the geometry of nickel(II) complexes of phosphine ligands than previously supposed.

Experimental

Diphenyl(*o*-methoxyphenyl)phosphine [12], *o*-chlorophenyldiphenylphosphine [14] and the cyclic phosphines (2) and (3) [15] were prepared as described in the literature. The complexes were prepared by the addition of a hot solution of nickel(II) bromide trihydrate (1 mol) in ethanol–acetic acid solution to a hot solution of the respective phosphine (2 mol), in acetic acid. On cooling, the complexes crystallised and were filtered off, washed with acetic acid, and allowed to air-dry.

New compounds prepared are as follows: *Dibromobis(*o*-chlorophenyldiphenylphosphine)nickel(II),* dull green crystals. Found: C, 53.35, H, 3.5; $C_{36}H_{28}Br_2Cl_2NiP_2$ requires C, 53.25, H, 3.45%; diamagnetic; *Dibromobis(diphenylo-methoxyphenylphosphine)nickel(II),* emerald green cyrstals. Found: C, 56.3, H, 4.25; $C_{38}H_{34}Br_2NiO_2P_2$ requires C, 56.8, H, 4.25%; μ_{eff} = 3.6 B.M; *Dibromobis(10-phenylphenothiaphosphine-5,5-dioxide)nickel(II),* dark brown crystals. Found: C, 50.8, H, 3.05; $C_{36}H_{26}Br_2NiO_4P_2S_2$ requires C, 49.9, H, 3.0%; diamagnetic; *Dibromotris(10-phenylphenothiaphosphine)nickel(II),* olive green crystals. Found: C 59.3, H, 4.73; $C_{54}H_{39}Br_2NiP_3S_3$ requires C, 59.2, H, 3.56%; diamagnetic.

Details of the diffuse reflectance spectra (recorded on an SP700 instrument, using MgO as diluent and reference) are in the Table.

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