

## TWO NEW METHYLNICKEL COMPOUNDS

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### Abstract

Tris(dimethylphenylphosphine)dimethylnickel(II) and bis(dimethylphenylphosphine)methylphenoxynickel(II) have been prepared and characterized.

The use of mixtures of nickel salts and alkylmetallic compounds (generally alkylaluminium or alkyl lithium compounds) as catalysts for olefin or acetylene oligomerization heralded the later isolation<sup>1-4</sup> of alkylnickel(II) compounds containing 2,2'-dipyridyl or organophosphines as stabilizing ligands. Later still,  $\text{Me}_2\text{Ni}\{\text{P}(\text{ch})_3\}_2$  and  $\text{Me}(\text{acac})\text{NiP}(\text{ch})_3$  ( $\text{ch}$  = cyclohexyl) were isolated as intermediates in the preparation of the nickel(0) dinitrogen complex  $\{(\text{ch})_3\text{P}\}_2\text{NiN}\equiv\text{NNi}\{\text{P}(\text{ch})_3\}_2$ .<sup>5</sup> Two new methylnickel(II) compounds,  $\text{Me}_2\text{Ni}(\text{PMe}_2\text{Ph})_3$  and  $\text{Me}(\text{PhO})\text{Ni}(\text{PMe}_2\text{Ph})_2$ , are now described.<sup>†</sup>

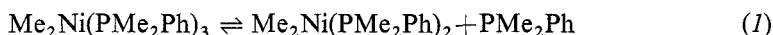
The p.m.r. spectra of  $\text{Me}_2\text{Ni}(\text{PMe}_2\text{Ph})_3$  and  $\text{Me}(\text{PhO})\text{Ni}(\text{PMe}_2\text{Ph})_2$  are shown in Table 1. The sharp Me-Ni singlet for either compound is consistent with a rapid

TABLE 1

P.M.R. SPECTRA OF METHYLNICKEL COMPLEXES IN PERDEUTEROBENZENE AT ROOM TEMPERATURE  
All integral ratios were consistent with the proposed formulae

Compound	$\text{CH}_3\text{-Ni}$	$\text{CH}_3\text{-P}$	Aromatic protons
$\text{Me}_2\text{Ni}(\text{PMe}_2\text{Ph})_3$	-0.65 (s)	1.04 (d, $J$ 5.6 Hz)	7.12 (m)
$\text{Me}(\text{PhO})\text{Ni}(\text{PMe}_2\text{Ph})_2$	-1.03 (s)	1.17 (s, broad)	7.40 (m)

interchange of phosphine ligands at ambient temperature, perhaps by a dissociative mechanism. The low apparent molecular weight (369; by cryometry in benzene) for  $\text{Me}_2\text{Ni}(\text{PMe}_2\text{Ph})_3$  is also consistent with appreciable dissociation as in (I):<sup>‡</sup>



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<sup>†</sup> Note added in proof.— $\text{Me}_2\text{Ni}(\text{PMe}_3)_2$  and  $\text{Me}_2\text{Ni}(\text{PMe}_3)_3$  have recently been prepared; see Klein, H. F., and Karsch, H. H., *Chem. Ber.*, 1972, **105**, 2628.

<sup>‡</sup> Evidence for equilibrium (I) could not be obtained by u.v. spectroscopy owing to strong absorption bands of excess phosphine.

<sup>1</sup> Yamamoto, T., Yamamoto, A., and Ikeda, S., *J. Am. chem. Soc.*, 1971, **93**, 3350.

<sup>2</sup> Green, M. L. H., and Smith, M. J., *J. chem. Soc. (A)*, 1971, 639.

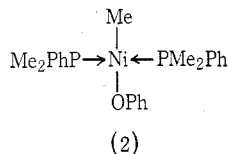
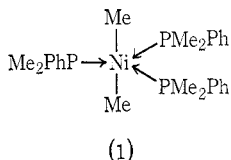
<sup>3</sup> Wilke, G., and Jonas, K., *Angew. Chem. int. Edn*, 1969, **8**, 519.

<sup>4</sup> Wilke, G., and Herrman, G., *Angew. Chem. int. Edn*, 1966, **5**, 581.

<sup>5</sup> Jolly, P. W., Jonas, K., Krüger, C., and Tsay, Y.-H., *J. organomet. Chem.*, 1971, **33**, 109.

By contrast the apparent molecular weight (417; by ebulliometry in benzene) for  $\text{Me}(\text{PhO})\text{Ni}(\text{PMe}_2\text{Ph})_2$  is close to the expected value.

At  $-75^\circ$  in toluene, the  $\text{Me-Ni}$  resonance of  $\text{Me}_2\text{Ni}(\text{PMe}_2\text{Ph})_3$  is a 1 : 3 : 3 : 1 quartet ( $J$  12 Hz), suggesting a trigonal bipyramid structure, (1).<sup>\*</sup> Low-temperature p.m.r. spectra of  $\text{Me}(\text{PhO})\text{Ni}(\text{PMe}_2\text{Ph})_2$  showed broadening of the  $\text{Me-Ni}$  resonance



but no splitting. The phenoxide probably has a square planar structure, for which *cis* and *trans* forms are possible. Where unidentate phosphine ligands have been used,  $\text{MeXNi}(\text{PR}_3)_2$  compounds usually have the *trans* configuration.<sup>2</sup> Thus *trans* structure (2) is more probable than the alternative *cis* structure.

### Experimental

Air was rigorously excluded from reactions by means of dry argon or nitrogen, and products were handled in Schlenk tubes or a small glove box. Solvents were refluxed over lithium aluminium hydride, then distilled.

P.m.r. spectra were measured in p.p.m. with respect to TMS as zero using a Varian A60 spectrometer, and infrared spectra (KCl) were determined with a Perkin-Elmer 137 spectrometer.

C, H, and P microanalyses were performed by the Australian Microanalytical Service; Ni was determined by edta titration or (less accurately) by atomic absorption analysis (Varian AA5 spectrometer).

#### *Tris(dimethylphenylphosphine)dimethylnickel(II)*

Dimethylphenylphosphine (5.8 g) and anhydrous nickel acetylacetonate (2.6 g) in anhydrous ether (20 ml) gave a blue complex. To this at *c.*  $-60^\circ$  was added dropwise with stirring trimethylaluminum (1.45 g) in ether (5 ml). The stirred mixture was then allowed to warm up slowly and at  $10^\circ$  red-brown crystals separated. The solution was left at  $15^\circ$  for 10 min then at  $-18^\circ$  for  $1\frac{1}{2}$  hr and was then cooled to  $-40^\circ$ . The crystalline product was filtered, recrystallized from ether (35 ml), and dried under high vacuum to give *tris(dimethylphenylphosphine)dimethylnickel(II)* (3.5 g), which is unstable above  $60^\circ$  but can be stored in a deep-freeze for several months (Found: C, 62.1; H, 8.0; Ni, 11.5; P, 18.4.  $\text{C}_{26}\text{H}_{30}\text{NiP}_3$  requires C, 62.1; H, 7.8; Ni, 11.7; P, 18.5%. Molecular weight (by cryometry in benzene) 369. Monomer requires 503). Infrared: 3030, 2900, 1470w, 1405, 1280, 1170, 1135, 1065w, 1020w, 994w, 935, 900, 817, 829w, 743, 725, and  $695\text{ cm}^{-1}$ .

#### *Bis(dimethylphenylphosphine)methylphenoxynickel(II)*

One equivalent of phenol (0.104 g) in ether (3 ml) was added dropwise to a stirred solution of *tris(dimethylphenylphosphine)dimethylnickel* (0.56 g) at  $-20^\circ$ . The ether solvent was then evaporated by bubbling nitrogen through the solution at room temperature. The residual oil, when dissolved in hexane (15 ml), gave upon cooling bright yellow crystals of *bis(dimethylphenylphosphine)-methylphenoxynickel(II)*, which were separated, washed several times with very cold hexane, then dried under high vacuum (Found: C, 62.1; H, 6.8; Ni, 13.0; P, 13.6.  $\text{C}_{23}\text{H}_{30}\text{NiOP}_2$  requires C, 62.3; H, 6.8; Ni, 13.2; P, 14.0%. Molecular weight (by ebulliometry in benzene) 417. Monomer requires 440). Repeated recrystallization gave a less pure produce of apparent molecular weight between 360 and 400. Infrared: 3030, 2900, 1580, 1560sh, 1470, 1425, 1410sh, 1310sh, 1290, 1250w, 1170, 1150, 1095, 1055w, 980, 917, 905, 860, 842, 827, 755, 740, 714, 693,  $677\text{ sh cm}^{-1}$ .

\* A prototype for structure (1) is afforded by  $\text{Ni}(\text{CN})_2(\text{PMe}_2\text{Ph})_3$ .<sup>6</sup>

<sup>6</sup> Stalick, J. K., and Ibers, J. A., *Inorg. Chem.*, 1969, **8**, 1090.