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# TETRAKIS(TRIETHYLPHOSPHINE)NICKEL(0) AND RELATED COMPLEXES

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## Summary

The preparation, properties and some oxidative addition reactions of the trialkylphosphine complexes $(Et_3P)_4Ni$ and $(n\text{-}Bu_3P)_2Ni(1,5\text{-}C_8H_{12})$ are described.

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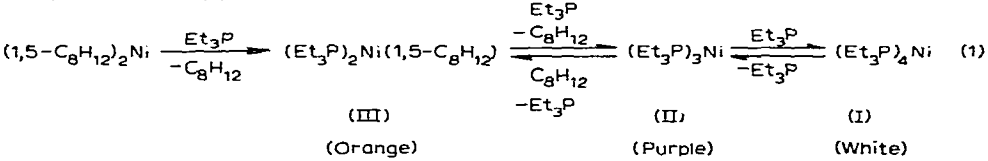
## Introduction

Considerable interest has recently been shown in trialkylphosphine complexes of low-valent transition metals [1 - 10]. The purpose of this paper is to describe a number of reactive nickel(0) derivatives which were prepared [11] as precursors to a series of fluorocarbon—nickel compounds [12 - 15]. The clean and facile route to $(Ph_3P)_4Ni$ by displacement of olefin from bis(1,5-cyclooctadiene)nickel(0) with triphenylphosphine has been described by Bogdanović, Kröner and Wilke [16]. $(Ph_2MeP)_4Ni$ [13], $(Me_3P)_4Ni$ [5,8] and $(H_3P)_4Ni$ [17] may be similarly prepared. Application of this synthesis to the trialkylphosphines $Et_3P$ and $n\text{-}Bu_3P$ reveals additional features of interest which form the basis of this report. $(Et_3P)_4Ni$ has been quoted as the reaction product from excess of $Et_3P$ and bis($\pi$-allyl)nickel [18], while $(Ph_3P)_2Ni(C_8H_{12})$, presumably analogous to $(n\text{-}Bu_3P)_2Ni(1,5\text{-}C_8H_{12})$ described below, has also been mentioned [19].

## Results and discussion

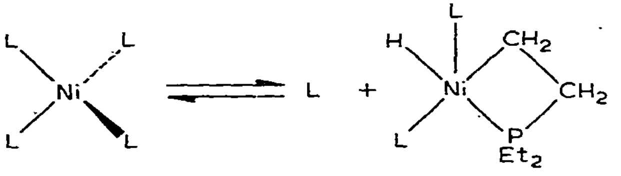
Addition of four molar equivalents of triethylphosphine to an ethereal suspension of bis(1,5-cyclooctadiene)nickel(0) in an argon atmosphere at room temperature gives an orange solution. On cooling, the colour fades and white crystals of $(Et_3P)_4Ni$ (I) appear; these changes are reversed on warming. Crystalline (I) may be isolated and dried at low temperature; warming to room temperature then causes no appreciable change. However, addition of solvent (hydrocarbon or ether) to the solid at room temperature produces an intense permanganate-purple solution. Cooling causes the colour to fade to orange at about −20° and white crystalline (I) is precipitated from the faintly yellow solution at −78°. The reverse changes occur on allowing the mixture to reattain room temperature. If 1,5-cyclooctadiene is added to the solution at room temperature the colour changes from purple to orange. On cooling, the colour fades to give (I) as before and this change, also, is reversible. These interesting variations are explained as follows (eqn. 1). With 1,5-cyclooctadiene in the solution, the nickel is present largely as (III). Cooling causes precipitation of the least soluble component, (I). In solution, pure (I) dissociates to give (II), although, on cooling, the less soluble (I) again crystallises. Dissociation of an $L_4Ni$ compound to give a more strongly coloured $L_3$ species has been observed for $[(o\text{-}CH_3C_6H_4{-}O)_3P]_4Ni$ [5]. Bright violet crystals of $[(C_6H_{11})_3P]_3Ni$ have been described [1] [although $\{(n\text{-}Bu)_3P\}_4Ni$ is reported to be deep violet [20]].



$$(1,5\text{-}C_8H_{12})_2Ni \xrightarrow[-C_8H_{12}]{Et_3P} \underset{\substack{(III)\\(Orange)}}{(Et_3P)_2Ni(1,5\text{-}C_8H_{12})} \xrightleftharpoons[\substack{C_8H_{12}\\-Et_3P}]{\substack{Et_3P\\-C_8H_{12}}} \underset{\substack{(II)\\(Purple)}}{(Et_3P)_3Ni} \xrightleftharpoons[-Et_3P]{Et_3P} \underset{\substack{(I)\\(White)}}{(Et_3P)_4Ni} \qquad (1)$$

Solid tetrakis(triethylphosphine)nickel(0) is pyrophoric. A solution in light petroleum rapidly and exothermically absorbed 2.9 molar equivalents (NTP) of dioxygen on shaking with an excess of the gas and $Et_3P{=}O$ was recovered (in 77% yield). Solutions of (I) undergo a variety of oxidative addition reactions, e.g. (*i*) with $I_2$ to give $(Et_3P)_2NiI_2$; (*ii*) with MeI to give $(Et_3P)_3NiI$ [see Experimental section, and ref. 21]; (*iii*) with $C_2F_4$ to give $(Et_3P)_2\overline{NiCF_2CF_2CF_2CF_2}$ [14]; and (*iv*) with $(CF_3)_2CO$ to give $(Et_3P)_2\overline{Ni{-}O{-}C}(CF_3)_2$ [13]. The high nucleophilicity of (I) or its dissociation products is further demonstrated by the observation that solutions will react with molecular dinitrogen. The infrared spectrum of (I) in light petroleum under argon shows only the absorptions expected from a $Et_3P/Ni$ complex. Passage of gaseous dinitrogen results in a slight change of colour from purple to dark red and the appearance of a strong sharp band at 2077 $cm^{-1}$ in the infrared spectrum. Application of vacuum to the solution reverses these changes. Manometric experiments showed that the uptake of dinitrogen is very small, as expected for a system involving $Et_3P$ as a competing ligand. Although it is apparent that dinitrogen is reversibly coordinated, various attempts to isolate a crystalline nickel—dinitrogen complex were unsuccessful. Similar results have been reported by other workers who have, however, succeeded in isolating the compound $[(C_6H_{11})_3P]_2Ni(N{\equiv}N)Ni[P(C_6H_{11})_3]_2$ [1,22].

In view of the rather high electron density to be expected at the nickel atom in (I), some tendency towards intramolecular oxidative addition might have been anticipated, giving rise to an equilibrium as shown below (eqn. 2), analogous to that found for $(Me_2PCH_2CH_2PMe_2)_2Ru$ in the classic studies of Chatt and Davidson [23,24] and subsequently observed in other systems although most commonly involving aromatic C—H [25]. However, infrared and PMR spectra of (I) do not show absorptions attributable [26 - 28] to Ni—H, and the chemical reactions of (I) generally lack suggestion of hydridic activity. Possible β-hydrogen activation is shown by (I) only in its reaction with excess of $CCl_4$ to give $CHCl_3$ [$(Ph_2MeP)_4Ni$ reacts, but gives no $CHCl_3$] although a complex intermolecular reaction cannot be ruled out. Passage of gaseous dihydrogen through solutions of (I) causes a very weak band to appear at 1914 $cm^{-1}$ in the infrared spectrum, suggesting that a true hydride may exist under appropriate conditions. Compounds formulated as $(R_3P)_2Ni(N_2)H$ [R = Et, $\nu(N_2)$ 2076 vs, $\nu(Ni—H)$ 1914 m $cm^{-1}$ (hexane); R = n-Bu, $\nu(N_2)$ 2074 vs, $\nu(Ni—H)$ 1914 s $cm^{-1}$ (Nujol)] have been described by Srivastava and Bigorgne, although they were incompletely characterised [29] while other unspecified complexes have also been mentioned [30]. Complex (I) will not act as a homogeneous hydrogenation catalyst for cyclohexene or tolan at room temperature and atmospheric pressure.



(2)

($L = Et_3P$)

An interesting sidelight on the equilibrium mentioned earlier (eqn. 1) is provided by the reaction of $n\text{-}Bu_3P$ with $(1,5\text{-}C_8H_{12})_2Ni$ under similar conditions, since in this case the yellow pyrophoric olefin complex $(n\text{-}Bu_3P)_2Ni(1,5\text{-}C_8H_{12})$ (IV) is precipitated. Solutions of (IV) show no interaction with gaseous dinitrogen in their infrared spectra. The 1,5-cyclooctadiene ligand in (IV) can be replaced by the chelating diphosphine $Ph_2PCH_2CH_2PPh_2$ to yield $(n\text{-}Bu_3P)_2Ni(Ph_2PCH_2CH_2PPh_2)$ (V) which is useful as a petroleum-soluble source of the $[(Ph_2PCH_2CH_2PPh_2)Ni]$ unit [e.g. (V) with $C_2F_4$ gave [14] $(Ph_2PCH_2CH_2PPh_2)\overline{NiCF_2CF_2CF_2CF_2}$]. The preparation of the much less soluble $(Ph_2PCH_2CH_2PPh_2)_2Ni$ from the diphosphine and $(1,5\text{-}C_8H_{12})_2Ni$ provides an alternative to the original [31] preparation from $Ni(CO)_4$. Reaction of (IV) with $C_2F_4$ gave $(n\text{-}Bu_3P)_2\overline{NiCF_2CF_2CF_2CF_2}$ [14].

## Experimental

Experimental procedures and measurements were as described previously [13 - 15]. Argon or dinitrogen atmospheres (as appropriate) were employed throughout. Nickel analyses were obtained by EDTA titration [32] after degradation (aqua regia) to $Ni^{2+}$. An iodine analysis was obtained by degradation (NaOH) to $I^-$ and titration of liberated ($Br_2$) iodine. The product from (9) was analysed commercially.

### *(1) Preparation of tetrakis(triethylphosphine)nickel(0), (I)*

A solution of triethylphosphine (2.90 g, 24.4 mmol) in ether (5 ml) was added dropwise to a stirred suspension of bis(1,5-cyclooctadiene)nickel(0)

[16] (1.68 g, 6.11 mmol) in ether (10 ml) at 20°. The resulting orange solution was cooled to $-78°$ and (at $-78°$) the white product washed with ether (10 ml), light petroleum (2 × 10 ml), and pumped dry to give crystalline (I) (2.62 g, 81%) (Found: Ni, 11.0. $C_{24}H_{60}NiP_4$ calcd.: Ni, 11.0%.) Infrared spectrum (light petroleum): 1411 m, 1314 w, 1239 m, 1386 w, 1116 m, 1040 s, 1019 vs, 994 m, 984 m, 962 m, 757 vs, 743 s, 716 s, 693 m, 675 m, 655 s $cm^{-1}$.

### *(2) Preparation of bis(tri-n-butylphosphine)(1,5-cyclooctadiene)nickel(0), (IV)*

Similarly, bis(1,5-cyclooctadiene)nickel(0) (2.68 g, 9.75 mmol) in ether (20 ml) was treated with tri-n-butylphosphine (7.90 g, 39.0 mmol) in ether (10 ml). The liquid volume was then reduced to 10 ml and the resulting yellow solid dissolved in light petroleum (50 ml). Reduction of the solution volume to 10 ml gave yellow crystals which were separated and washed with light petroleum (2 × 5 ml) to yield (IV) (2.93 g, 53%), m.p. 102 - 104° (Found: Ni, 10.3. $C_{32}H_{66}NiP_2$ calcd.: Ni, 10.3%.) Infrared spectrum (Nujol): 1314 w, 1293 w, 1271 vw, 1224 vw, 1213 vw, 1196 m, 1165 w, 1143 vw, 1085 s, 1080 s, 1044 w, 1033 m, 1002 m, 969 w, 922 vw, 897 s, 883 m, 866 vw, 845 vw, 763 s, 719 s, 684 vw $cm^{-1}$. PMR spectrum ($C_6F_6$): $\tau$ 4.61 (4H, s), 7.71 (8H, s), 8.39 (36H, m) and 8.93 ppm (18H, m).

### *(3) Preparation of bis(tri-n-butylphosphine)[1,2-bis(diphenylphosphino)-ethane] nickel(0), (V)*

1,2-Bis(diphenylphosphino)ethane (0.378 g, 0.950 mmol) in benzene (5 ml) was added dropwise to a stirred solution of (IV) (0.543 g, 0.950 mmol) in light petroleum (20 ml). All material volatile at room temperature was then removed in vacuo ($10^{-3}$ mmHg), and the residue extracted with light petroleum (30 ml). Solvent was removed (10 mmHg), the residual red oil crystallised (−63°), and the product pumped dry at 20° to yield (V) as a red-brown solid (0.490 g, 60%), dec. 130°. (Found: Ni, 6.5. $C_{50}H_{78}NiP_4$ calcd.: Ni, 6.8%.) Infrared spectrum (Nujol): 1584 w, 1478 m, 1430 s, 1301 w, 1269 vw, 1228 vw, 1211 vw, 1195 vw, 1170 w, 1087 m, 1063 vw, 1041 vw, 1021 w, 998 vw, 963 w, 890 m, 859 w, 838 vw, 790 w, 763 vw, 737 m, 727 s, 714 m, 687 s, 647 m $cm^{-1}$. PMR spectrum ($CH_2Cl_2$): $\tau$ 2.71 (20H, m), 7.8 ($\approx$ 4H, masked), 8.43 (36H, m) and 9.06 ppm (18H, m).

### *(4) Preparation of bis[1,2-bis(diphenylphosphino)ethane] nickel(0) from bis (1,5-cyclooctadiene)nickel(0)*

Bis(1,5-cyclooctadiene)nickel(0) (0.600 g, 2.18 mmol) and bis(1,2-diphenylphosphino)ethane (1.74 g, 4.36 mmol) were vigorously stirred together in ether (60 ml) at room temperature. After 1 h, the solution volume was reduced to 3 ml and the precipitate recrystallised from benzene (5 ml) by addition of light petroleum (20 ml) to give the required complex [31] (1.55 g, 83%).

### *(5) Reaction of (I) with carbon tetrachloride*

(I) (0.087 g) was treated with carbon tetrachloride (1.0 ml), immediate and vigorous reaction taking place. After a few minutes, the solvent was removed in vacuo and its IR and PMR spectra recorded; the presence of chloroform was proved by comparison with an authentic $CHCl_3/CCl_4$ mixture. A similar experiment using tetrakis(methyldiphenylphosphine)nickel(0) [13] showed a less vigorous reaction with $CCl_4$ and yielded no $CHCl_3$.

*(6) Reaction of (I) with iodine*

A solution of iodine (0.180 g, 0.709 mmol) in ether/pentane (1/2 v/v) was added dropwise to a stirred solution of (I) (0.300 g, 0.564 mmol) in pentane (5 ml). Crystallisation (— 78°) gave *trans*-$(Et_3P)_2NiI_2$ (0.240 g, 78%) m.p. 91 - 92° (lit. [33] 91 - 92°). (Found: C, 26.3; H, 5.5.$C_{12}H_{30}I_2NiP_2$ calcd.: C, 26.3; H, 5.5%.)

A similar experiment in a sealed tube using iodotrifluoromethane (4 molar equivalents) in place of iodine also gave *trans*-$(Et_3P)_2NiI_2$ as the only isolable product (24%).

*(7) Reaction of (I) with iodomethane*

Iodomethane (0.070 g, 0.489 mmol) in light petroleum (5 ml) was similarly added to (I) (0.260 g, 0.489 mmol) in light petroleum (5 ml) at — 10°. Cooling (— 78°) gave bright yellow crystals which were recrystallised from light petroleum (3 ml) at — 78° and pumped dry at — 10° to yield paramagnetic iodotris(triethylphosphine)nickel(I) (0.200 g, 76%), m.p. ca. 40° (dec.), stable at or below — 10°. (Found: I, 22.9; Ni, 10.4. $C_{18}H_{45}INiP_3$ calcd.: I, 23.5; Ni, 10.9%.) For further details, see ref. 21.

*(8) Reaction of iodotris(triethylphosphine)nickel(I) with tetrafluoroethylene*

A solution of $(Et_3P)_3NiI$ (0.200 g, 0.370 mmol) in light petroleum (15 ml) was sealed in a Carius tube with tetrafluoroethylene (2.88 mmol) and set aside at 20° for 48 h. Yellow crystals of $(Et_3P)_2NiCF_2CF_2CF_2CF_2$ (0.084 g) precipitated. The deep green solution yielded the same compound (0.006 g, total yield 49%) together with *trans*-$(Et_3P)_2NiI_2$ (0.097 g, 48%) on cooling to — 78°.

*(9) Reaction of (IV) with iodotrifluoromethane*

A solution of (IV) (0.543 g, 0.949 mmol) in light petroleum (20 ml) was treated with iodotrifluoromethane (2.39 mmol) in a sealed Carius tube. All material volatile at 20°/$10^{-3}$ mmHg was removed from the resulting dark green solution. The residual oil was dissolved in light petroleum (1 ml) and methanol (10 ml) added slowly with very vigorous stirring. Cooling (— 78°) gave shining green-black crystals which were recrystallised twice more by the same method (yield 0.280 g) m.p. 35 - 37°. (Found: C, 43.5; H, 8.3; I, 23.6; Ni, 8.7. $C_{25}H_{54}F_3I_2NiP_2$ calcd.: C, 45.5, H, 8.3; I, 19.3; Ni, 8.9%. $C_{24}H_{54}I_2NiP_2$ calcd.: C, 40.2; H, 7.6; I, 35.4; Ni, 8.2%). The expected product, *trans*-$(n\text{-}Bu_3P)_2Ni(CF_3)I$, was thus present but contaminated with *trans*-$(n\text{-}Bu_3P)_2NiI_2$. The $^{19}F$ NMR spectrum ($C_6H_6$) of the mixture showed Ni—$CF_3$ at 8.4 ppm relative to $CFCl_3$ with *J*(P—F) (between outer lines of virtual triplet) 42.0 Hz. See also ref. 21.

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## References

1 P.W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, J. Organometal. Chem., 33 (1971) 109.
2 P.W. Jolly, I. Tkatchenko and G. Wilke, Angew. Chem., Int. Ed. Engl., 10 (1971) 328.
3 M. Englert, P.W. Jolly and G. Wilke, Angew. Chem., Int. Ed. Engl., 11 (1972) 136.
4 J.M. Brown, B.T. Golding and M.J. Smith, Chem. Commun., (1971) 1240.
5 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
6 D.H. Gerlach, A.R. Kane, G.W. Parshall, J.P. Jesson and E.L. Muetterties, J. Amer. Chem. Soc., 93 (1971) 3543.
7 L.J. Guggenberger, A.R. Kane and E.L. Muetterties, J. Amer. Chem. Soc., 94 (1972) 5665.
8 H.-F. Klein and H. Schmidbaur, Angew. Chem., Int. Ed. Engl., 9 (1970) 903.
9 H.-F. Klein and J.F. Nixon, Chem. Commun., (1971) 42.
10 H.-F. Klein, Angew. Chem., Int. Ed. Engl., 10 (1971) 343.
11 C.S. Cundy, Ph.D. Thesis, University of Bristol, 1969.
12 J. Browning, D.J. Cook, C.S. Cundy, M. Green and F.G.A. Stone, Chem. Commun., (1968) 929.
13 J. Browning, C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1969) 20.
14 C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1970) 1647.
15 J. Browning, C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1971) 448.
16 B. Bogdanovič, M. Kröner and G. Wilke, Justus Liebigs Ann. Chem., 699 (1966) 1.
17 M. Trabelski, A. Loutellier and M. Bigorgne, J. Organometal. Chem., 40 (1972) C45.
18 G. Wilke and B. Bogdanovič, Angew. Chem., 73 (1961) 756.
19 G. Wilke, E.W. Müller, M. Kröner, P. Heimbach and H. Breil, German Patent, 1191375 (1960).
20 E. Uhlig and H. Walther, Z. Chem., 11 (1971) 23.
21 C.S. Cundy and H. Nöth, J. Organometal. Chem., 30 (1971) 135.
22 P.W. Jolly and K. Jonas, Angew. Chem., Int. Ed. Engl., 7 (1968) 731.
23 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
24 U.A. Gregory, S.D. Ibekwe, B.T. Kilbourn and D.R. Russell, J. Chem. Soc. A, (1971) 1118.
25 G.W. Parshall, Accounts Chem. Res., 3 (1970) 139.
26 K. Jonas and G. Wilke, Angew. Chem., Int. Ed. Engl., 8 (1969) 519.
27 M.L.H. Green and T. Saito, Chem. Commun., (1969) 208.
28 M.L.H. Green, T. Saito and P.J. Tanfield, J. Chem. Soc. A, (1971) 152.
29 S.C. Srivastava and M. Bigorgne, J. Organometal. Chem., 18 (1969) P30.
30 J.B. Lee and B. Cubberly, Tetrahedron Lett., (1961) 1061.
31 J. Chatt and F.A. Hart, J. Chem. Soc., (1960) 1378.
32 H.A. Flaschka, EDTA Titrations, Pergamon, Oxford, 1959, p. 79.
33 K.A. Jensen, Z. Anorg. Allg. Chem., 229 (1936) 265.