Stable Methylnickel Complexes containing Tertiary Phosphine Ligands

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The preparation and properties of the complexes *trans*-$NiMeX(PPr^i_3)_2$ (I), where X = Cl, Br, or I, and $NiMe_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)$ (II) are described. The complexes (I) react with triphenylphosphine to give the complexes $NiX(PPh_3)_3$, X = Cl, Br, or I, and $NiMeI(PPr^i_3)_2$ reacts with methyl iodide to give $[PPr^i_3Me][NiI_3PPr^i_3]$. Complex (II) reacts with phenol to give the phenoxy-derivative $Ni(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)Me(OPh)$.

SQUARE-PLANAR alkyl- and hydrido-nickel derivatives of the type $NiR^1X(PR^2_3)_2$, where R^1 = alkyl or H and R^2 is a primary alkyl group, are generally very unstable thermally and not isolable.[1,2] However, recently thermally stable hydride derivatives *trans*-$NiHX(PR_3)_2$ have been isolated where R was a secondary alkyl group, such as cyclohexyl or isopropyl.[3] We have investigated the preparation of analogous methyl derivatives in the anticipation that they would also have an enhanced thermal stability. This work is described here. During the course of these studies the alkyl derivative $NiHMe(PR_3)_2$, where R = cyclohexyl, was reported. This was prepared by the reaction of trimethylaluminium with the hydride complex $NiH(O{\cdot}CO{\cdot}Me)(PR_3)_2$.[4]

Preparation and Properties.—The dichloride *trans*-$NiCl_2(PPr^i_3)_2$ reacts in ether with methyl-lithium at −78 to −10°; isolation at low temperature gives the methyl derivative *trans*-$NiMeX(PPr^i_3)_2$, (I; X = Cl) as very air-sensitive, yellow crystals. The ^1H n.m.r. and analytical data are given in the Table.

^1H n.m.r. and analytical data

Compounds	Colour	M.p./°C	^1H n.m.r. data[a]	Found (reqd.) (%) C	H	Ni
trans-$NiMeCl(PPr^i_3)_2$	Yellow	—	10·8,[b] t[c] (J_{PH} = 8),NiMe	51·9 (53·1)	10·1 (10·5)	14·0 (13·7)
trans-$NiMeBr(PPr^i_3)_2$	Yellow	82[d]	10·3,[b] t[c] (J_{PH} = 8), NiMe	47·3 (48·2)	9·1 (9·5)	12·7 (12·5)
trans-$NiMeI(PPr^i_3)_2$	Brown	69[d]	—	42·4 (43·8)	8·0 (8·6)	11·5 (11·3)
cis-$NiMe_2$(diphos)	Yellow	130 (decomp.)	8·2,[e] d[f] (16·0[g]), $P{\cdot}CH_2{\cdot}CH_2{\cdot}P$ 8·2[h] 9·2, d[f] (5·9[g]), NiMe 9·2, d[i] (12·8[g]), NiMe	68·9 (69·0)	6·1 (6·2)	12·2 (12·1)
cis-NiMe(OPh)(diphos)	Orange	150 (decomp.)	10·2,[j] t[k] (J_{PH} = 5·2), NiMe	70·5 (70·2)	6·0 (5·7)	10·5 (10·4)
$[PPr^i_3Me][NiI_3(PPr^i_3)]$	Red	—	—	29·7 (29·4)	5·7 (5·8)	7·9 (7·6)

[a] Data are given as chemical shift, τ, multiplicity (Hz), assignment. All spectra showed complex bands assignable to the hydrocarbons of the tertiary phosphine ligands. [b] In dimethyl ether at 0 °C. [c] Triplet. [d] Melts with decomposition. [e] In $[^2H_6]$-benzene. [f] Doublet. [g] See Discussion. [h] Extremely broad doublet. [i] Broad doublet. [j] In $[^2H_6]$dimethyl sulphoxide (low solubility). [k] A broad triplet, which does not show a 1 : 2 : 1 intensity distribution.

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The crystalline complex (I; X = Cl) is slowly decomposed (weeks) in an inert atmosphere at room temperature but appears to be indefinitely stable at −6°. It is very soluble in the less polar organic solvents, such as benzene, but the solutions decompose slowly at room temperature and usually a nickel mirror is deposited within a few hours. Generally it is most convenient to handle solutions of compounds (I) in cold diethyl ether (0°). All solutions are decomposed almost immediately in air.

The complex (I; X = Br) was prepared from the corresponding dibromide derivative and methyl-lithium which was prepared from methyl bromide, whilst the iodide (I; X = I) was formed when the dichloride was treated with methyl-lithium which had been prepared by use of methyl iodide. It therefore appears that the presence of the excess of iodide in the methyl-lithium solution causes metathetical displacement of the chloride.

It has been reported that treatment of the compound $NiBr_2$(diphos), where diphos is $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, with methylmagnesium bromide gives a very unstable derivative, either the dimethyl or methyl bromide NiMeX(diphos), X = Me or Br, but the compound could not be characterized.[5] We have found that the chloride $NiCl_2$(diphos) reacts with methyl-lithium at 0° to give the dimethyl derivative $NiMe_2$(diphos) (II) in good yields as yellow crystals. The stoicheiometry and structure of the complex (II) are deduced from the data given in the Table and Experimental section.

The dimethyl derivative (II) is sparingly soluble in ether but freely soluble in benzene. The solutions are stable at room temperature but are rapidly decomposed on exposure to air. The crystals may be safely handled in air for brief periods (30 min).

Chemical Properties.—The complex (I; X = I) reacts immediately with methyl iodide in ether with precipitation of lustrous red crystals of stoicheiometry $[PPr^i_3Me][NiI_3PPr^i_3]$. Complex anions of the type $[NiX_3PR_3]^-$ are well known,[6] although this particular anion has not been described previously.

All the complexes (I; X = Cl, Br, or I) react with triphenylphosphine in ether, to give yellow-orange crystalline compounds, which, by analysis and comparison with published data,[7,8] are the complexes $NiX(PPh_3)_3$, X = Cl, Br, or I.

Finally the complex (I; X = Br) has been shown to be a very good catalyst for the polymerization of acetylene.

Wilke has shown that the bipyridyl (bipy) complex $NiEt_2$(bipy) reacts with phenol forming a stable derivative NiEt(OPh)(bipy).[9] We have found that the complex (II) reacts similarly with phenol forming a stable orange crystalline derivative which analysis, ^{1}H n.m.r. and i.r. spectra show to be NiMe(OPh)(diphos).

This complex is stable for prolonged periods in air but is rapidly oxidized in solution.

DISCUSSION

The ^{1}H n.m.r. data are given in the Table. The assignments for the complexes (I; X = Cl or Br) are unambiguous and show that the methyl hydrogen atoms couple equally with the two ^{31}P nuclei giving a triplet, $J_{PH} = 8$ Hz.

The spectrum of the dimethyl derivative (II) is more complicated. The bands at τ 8 and 9 are the X spectra of an $X_2AA'X_2'$ and $X_3AA'X_3'$ system respectively and each consists of a sharp doublet within a very broad doublet. This type of spectrum has been described elsewhere.[10] On the basis of this assignment, J_{AX} and $J_{AX'}$ (where X = H of methyl group), appear to have opposite sign, *e.g.* $J_{AX} = 10{\cdot}1$ and $J_{AX'} = -4{\cdot}1$ Hz.

The enhanced thermal stability of the methyl complexes (I) in comparison with the n-alkylphosphine analogues seems most likely to arise through steric effects, as discussed for the hydride analogues.[3]

EXPERIMENTAL

All preparations and reactions were carried out in the complete absence of oxygen, usually under argon. Nickel analyses were performed by use of an atomic absorption spectrophotometer and weighings were carried out under argon. The weighings for the C,H analyses were, through necessity, performed rapidly in air but slight oxidation was observed which presumably accounts for some values being outside normally acceptable limits (*ca.* 2% low). ^{1}H n.m.r. spectra were determined with a JEOL instrument at 60 MHz.

trans-*Chloro(methyl)bis(tri-isopropylphosphine)nickel*.—*trans*-Dichlorobis(tri-isopropylphosphine)nickel (1·5 g, 0·0033 mol) in dry ether (120 ml) was treated with methyl-lithium prepared from lithium and methyl chloride (7·7 ml of 0·64M. 0·0050 mol) at −78° with stirring. The mixture was allowed to warm to −5° over a period of 24 h. Cold deoxygenated water was added to the mixture (30 ml). The aqueous layer was frozen and the supernatant ethereal layer was separated, dried (anhydrous sodium sulphate) at 0°, and filtered. The solvent was removed *in vacuo* at −10° until the yellow crystals began to separate. Further yellow crystals were then obtained by cooling slowly to −78°. The product was recrystallized from pure ether at −78°, the yellow crystals were washed with cold ether and dried *in vacuo* (yield 65%). The analogous complexes (I; X = Br or I) were prepared similarly by reactions between $NiX_2(PPr^i_3)_2$ and ethereal solutions of LiMe and LiX′ where $X_2 = X' =$ Br for the bromide and where $X_2 =$ Cl and X′ = I for the iodide.

Bis-1,2-(*diphenylphosphino*)*ethanedimethylnickel*.—Dichloro-1,2-(diphenylphosphino)ethanenickel (4·1 g, 0·0080 mol) in ether (500 ml) was treated with methyl-lithium (24 ml of 1M. 0·024 mol) at 0° with stirring. After 24 h the mixture was hydrolysed and the product was isolated as described above (yield 50%).

Reaction between Methyl Iodide and trans-*Iodo*(*methyl*)*bis*(*tri-isopropylphosphine*)*nickel*.—Addition of excess of methyl

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iodide to a cold (0°) solution of *trans*-NiMeI(PPr^i_3)$_2$ (0·5 g) in ether gave an immediate reaction and red analytically pure crystals of [PPr^i_3Me][$NiI_3PPr^i_3$] were precipitated.

Reaction between Triphenylphosphine and trans-NiMeX(PPr^i_3)$_2$, X = Cl, Br, or I.—Excess of triphenylphosphine in ether solution was added to a cold solution of the methylnickel complex in ether. Within minutes the *compound* crystallized from the solution and required no further purification, after washing and drying [Found: C, 74·1; H, 5·0. NiCl(PPh_3)$_3$ requires C, 73·7; H, 5·2%. Found: C, 69·9; H, 4·9; Ni, 6·4. NiBr(PPh_3)$_3$ requires C, 70·1; H, 4·9; Ni, 6·4%. Found: C, 65·5; H, 4·8. NiI(PPh_3)$_3$ requires C, 66·5; H, 4·7%].

Bis-1,2-(*diphenylphosphino*)*ethanemethylphenoxynickel*.—The compound 1,2-(diphenylphosphino)ethanedimethylnickel (0·20 g) in (20 ml) 50/50 benzene : ether was treated with phenol (0·06 g). Within 10 min orange crystals were deposited and a gas was evolved. The crystals of NiMe(OPh)(diphos) were washed with ether and dried *in vacuo* to give the pure compound (yield 75%).

We wish to thank Deutsche Advance Produktion for a generous gift of tri-isopropylphosphine and we acknowledge the S.R.C. for financial support (to M. J. S.).

[0/1334 *Received, August 3rd*, 1970]