# Complexes of Nickel(II), Palladium(II), and Platinum(II) with the β-Ketophosphines $PBu^t_2(CH_2COR)$ (R = Ph or $Bu^t$) †

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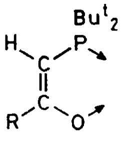
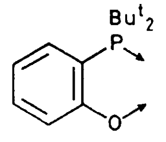
The β-ketophosphines $PBu^t_2(CH_2COR)$ (R = Ph or $Bu^t$) have been prepared by treating the α-bromoketones $BrCH_2COR$ with $PBu^t_2H$ and subsequent treatment with base. With hydrated nickel(II) chloride, complexes of the type *trans*-$[Ni\{Bu^t_2PCH{=}C(O)R\}_2]$, in which the nickel is chelated by the tertiary phosphine enolate ion, are formed rapidly. In contrast, with $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCPh)_2]$ these β-ketophosphines, even on prolonged boiling in alcohols, give complexes of type *trans*-$[MCl_2\{PBu^t_2(CH_2COR)\}_2]$. However, when these chloro-complexes are treated with sodium 2-methoxyethoxide, ring closure occurs to give the bis(chelates) *trans*-$[M\{Bu^t_2PCH{=}C(O)R\}_2]$. Proton and $^{31}P$ n.m.r. and i.r. data are given.

WE and others have shown that bulky tertiary phosphine ligands generate unusual chemistry with transition metals; we have been particularly interested in the effects of the $Bu^t_2P$ group.[1] Coupled with this has been an interest in the effects of functional substituents, *e.g.* esters,[2] phenols,[3] ethers,[4,5] and crown ethers,[6] on the properties of tertiary phosphine ligands. We now describe two new tertiary β-ketophosphines $PBu^t_2(CH_2COPh)$ (Q) and $PBu^t_2(CH_2COBu^t)$ (Q′) and their behaviour with nickel(II), palladium(II), and platinum(II) chlorides. We anticipated that these ligands could be unidentate (through phosphorus), possibly bidentate with a further interaction of the keto-group, or that they could lose a proton to give a bidentate enolate ion of type (1; R = Ph), represented as P–O or (1; R = $Bu^t$), represented as P′–O. This chelate system would have a formal similarity to the chelate of type (2), from which some unusual complexes were prepared.[4,5] β-Ketophosphines do not seem to have been investigated as ligands, although Carty *et al.*[7] showed that mild hydrolysis of *cis*-$[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$ produced a mixture of complexes from which the compounds $[Pd\{Ph_2PCH{=}C(O)CF_3\}_2]$, $[PdCl\{Ph_2PCH{=}C(O)CF_3\}\{PPh_2(OH)\}]$, and $[PdCl\{Ph_2PCH{=}C(O)CF_3\}\{PPh_2(OEt)\}]$ were isolated. We have also made some rhodium and iridium complexes containing the ligand (1; R = Ph) produced by alkoxide attack on co-ordinated $PBu^t_2(C{\equiv}CPh)$ followed by elimination of alkyl halide.[8]



(1)



(2)

## RESULTS AND DISCUSSION

*Preparation of the β-Ketophosphines*.—They were prepared *via* the phosphonium salts, $[PBu^t_2(CH_2COR)H]Br$, formed by treating $PBu^t_2H$ with $BrCH_2COR$ in acetone. Subsequent treatment of these phosphonium salts with sodium acetate gave the required phosphines as distillable liquids which were characterized as their quaternary salts with methyl iodide. Details are in the Experimental section and characterizing data in Table 1.

*Interaction of the β-Ketophosphines with Nickel*(II), *Palladium*(II), *or Platinum*(II) *Chlorides*.—Addition of $PBu^t_2(CH_2COBu^t)$ (Q′) to an ethanolic solution of nickel(II) chloride rapidly gave the orange-yellow chelate complex *trans*-$[Ni\{Bu^t_2PCH{=}C(O)Bu^t\}_2]$, *i.e.* $[Ni(P'{-}O)_2]$. Characterizing microanalytical and molecular-weight data are in Table 2. The *trans* configuration follows from the occurrence of a t-butyl triplet pattern with $^3J(PH) + {}^5J(PH) = 13.3$ Hz in the $^1H$ n.m.r. spectrum (Table 3). The ethene proton also gives a triplet pattern with $^2J(PH) + {}^4J(PH) = 4.0$ Hz and the $^{31}P$ signal was a singlet. The corresponding complex from $PBu^t_2(CH_2COPh)$, *viz.* $[Ni(P{-}O)_2]$, was too insoluble for n.m.r. studies but very probably also has the *trans* configuration. Both complexes were very stable and sublimed without decomposition on a Kofler hot-stage. Palladium and platinum chlorides behaved differently from nickel in that even after refluxing $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCPh)_2]$ with $PBu^t_2(CH_2COR)$ (R = $Bu^t$ or Ph) in ethanol for 30 min only complexes of type *trans*-$[MCl_2\{PBu^t_2(CH_2COR)\}_2]$ (M = Pd or Pt) were formed. The microanalytical and molecular-weight data are in Table 2. The *trans* configurations again follow from the t-butyl triplet patterns in the $^1H$ n.m.r. spectra and the presence of a single but strong band within the range 329—347 $cm^{-1}$ due to ν(M–Cl) and typical of a *trans* Cl–M–Cl moiety. A strong band due to ν(C=O) within the range 1 690—1 720 $cm^{-1}$ was also observed in the i.r. spectra. The $^{31}P$ n.m.r. spectra showed a broad singlet (with satellites for the platinum complex due to $^{195}Pt$). The broadness is probably caused by restricted rotation around the phosphorus–metal bonds due to interaction between the bulky $PBu^t_2$ groups and the chlorine ligands in *cis* position,[9] although we did not confirm this by a study at different temperatures.

These complexes *trans*-$[MCl_2Q_2]$ or *trans*-$[MCl_2Q'_2]$ were recovered unchanged after being heated under reflux in 2-methoxyethanol for 30 min. However, in the presence of sodium 2-methoxyethoxide (2.5 equiva-

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† No reprints available.

TABLE 1

Microanalytical, i.r., $^1$H n.m.r., and $^{31}$P n.m.r. data for the tertiary phosphines and phosphonium salts

| | Analysis (%) [a] | | | I.r. (cm$^{-1}$)[b] | N.m.r. | |
|---|---|---|---|---|---|---|
| Compound | C | H | Halogen | $\nu$(CO) | $^1$H [c] δ(Bu$^t$)/p.p.m. | $^{31}$P [d] δ/p.p.m. |
| [PBu$^t_2$(CH$_2$COPh)H]Br | 55.4 (55.7) | 7.6 (7.6) | 23.5 (23.15) | | | |
| [PMeBu$^t_2$(CH$_2$COPh)]I | 50.3 (50.25) | 6.9 (6.95) | 31.1 (31.25) | 1 674 | 1.62 (16) [e] | |
| [PMeBu$^t_2$(CH$_2$COBu$^t$)]I | 47.0 (46.65) | 8.3 (8.35) | 33.0 (32.85) | 1 695 | 1.56 (16) [f] | |
| PBu$^t_2$(CH$_2$COPh) | | | | | 2.0 (11) [g] | 30.6 |
| PBu$^t_2$(CH$_2$COBu$^t$) | | | | | 2.7 (11) [g] | 24.1 |

[a] Calculated values in parentheses. [b] Nujol mulls. [c] In CDCl$_3$ at 60 MHz and 34 °C; $^3J$(PH)/Hz in parentheses. [d] At 36.43 MHz in C$_6$D$_6$ at 27 °C; shifts relative to 85% H$_3$PO$_4$. [e] δ(CH$_2$) = 4.7 p.p.m., $^2J$ = 12 Hz; δ(Me) = 2.13 p.p.m., $^2J$ = 12 Hz. [f] δ(CH$_2$) = 4.3 p.p.m., $^2J$ = 11 Hz; δ(Me) = 2.5 p.p.m., $^2J$ = 12 Hz; δ(C*Bu*$^t$) = 1.35 p.p.m. [g] In C$_6$H$_6$.

TABLE 2

Microanalytical and molecular-weight data for the nickel, palladium, and platinum complexes

| | Analysis (%) [a] | | | |
|---|---|---|---|---|
| Complex | C | H | Cl | *M* [b,c] |
| [Ni(P–O)$_2$] | 66.05 (65.7) | 8.1 (8.25) | | insoluble |
| [Ni(P′–O)$_2$] | 61.1 (61.7) | 10.5 (10.35) | | 545 (545) |
| [PdCl$_2$Q$_2$] | 54.1 (54.45) | 7.35 (7.15) | 10.0 (10.1) | |
| [PdCl$_2$Q′$_2$] | 50.1 (50.1) | 8.7 (8.8) | 10.5 (10.65) | 654 (660) |
| [Pd(P–O)$_2$] | 61.15 (60.7) | 7.8 (7.65) | | |
| [Pd(P′–O)$_2$] | 56.75 (56.7) | 9.4 (9.5) | | 609 (593) |
| [PtCl$_2$Q$_2$] | 48.75 (48.4) | 6.5 (6.35) | 9.25 (8.9) | 771 (795) |
| [PtCl$_2$Q′$_2$] | 46.1 (46.45) | 7.95 (8.0) | 9.55 (9.8) | 763 (749) |
| [Pt(P–O)$_2$] | 53.35 (53.25) | 6.65 (6.7) | | |
| [Pt(P′–O)$_2$] | 49.35 (49.35) | 8.2 (8.3) | | 684 (682) |

[a] Q = PBu$^t_2$(CH$_2$COPh), Q′ = PBu$^t_2$(CH$_2$COBu$^t$), P–O = Bu$^t_2$PCH=C(O)Ph, P′–O = Bu$^t_2$PCH=C(O)Bu$^t$. [b] Calculated values in parentheses. [c] Recorded in chloroform solution.

TABLE 3

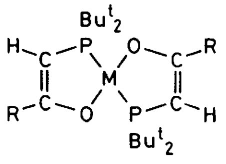
Proton and $^{31}$P n.m.r. and i.r. data for the metal complexes

| | $^1$H N.m.r. [a] | | | $^{31}$P N.m.r.[b] | | I.r. (cm$^{-1}$, Nujol mull) | | |
|---|---|---|---|---|---|---|---|---|
| Complex | δ(PBu$^t$) [c] | δ(CBu$^t$) | δ(CH$_2$) or δ(=CH) [d] | δ(H$_3$PO$_4$) | $^1J$(PtP) | $\nu$(C≡O) | $\nu$(C=C) + $\nu$(C–O) | $\nu$(M–Cl) |
| [Ni(P′–O)$_2$] | 1.49 (13.3) | 0.95 (s) | 3.63 (t) (4.0) | 48.4 | | | 1 515, 1 478 | |
| [PdCl$_2$Q$_2$] [e] | 1.59 (13.4) | | 3.79 (s) | 42.6 | | 1 692s | | 347s |
| [PdCl$_2$Q′$_2$] | 1.51 (13.2) | 1.21 (s) | 3.37 (s) | 37.9 | | 1 712s | | 342s |
| [Pd(P′–O)$_2$] | 1.36 (13.8) | 1.08 (s) | 3.65 (t) (5.9) | 65.6 | | | 1 511 | |
| [PtCl$_2$Q$_2$] | 1.58 (13.5) | | 3.77 (t) (6.0) | | | 1 690s | | 328s |
| [PtCl$_2$Q′$_2$] | 1.54 (13.4) | 1.26 (s) | 3.39 | 44.2 | 2 590 | 1 711s | | 329s |
| [Pt(P′–O)$_2$] | 1.36 (13.8) | 1.11 (s) | 3.79 (tt) (8.2) | 63.2 | 2 752 | | 1 517 | |

$^4J$(PtC*H*) = 35.3 Hz

[a] Spectra recorded at ambient temperature (*ca.* 25 °C) and 60 MHz in CDCl$_3$ solution unless indicated otherwise. δ ±0.02 p.p.m., $J$ ±0.2 Hz; t = triplet, tt = triplet of triplets, s = singlet. [b] At *ca.* 27 °C and 36.43 MHz in CDCl$_3$. Shifts relative to 85% H$_3$PO$_4$ (±0.1 p.p.m.), those to high field being positive; $J$ ±2 Hz. [c] All triplets; values of $^3J$(PH) + $^5J$(PH) in parentheses. [d] Values of $^2J$(PH) + $^4J$(PH) in parentheses. [e] In CH$_2$Cl$_2$.

lents per metal atom) the yellow chelate complexes *trans*-[$\overline{\mathrm{M(P{-}O}}\mathrm{)_2}$] and *trans*-[$\overline{\mathrm{M(P'{-}O}}\mathrm{)_2}$] (**3**; M = Pd or Pt; R = Ph or $\mathrm{Bu^t}$) were produced in good yield. The platinum complex *trans*-[$\overline{\mathrm{Pt\{Bu^t_2PCH{=}C(O}}\mathrm{)Bu^t\}_2}$] showed a triplet t-butyl pattern (Table 3) and the ethene proton also showed a triplet pattern with satellites [$\delta$ = 3.79 p.p.m., $^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})$ = 8.2 Hz, $^3J$(PtH) = 35.3 Hz]. The $^{31}$P resonance and satellites were sharp and the value of $^1J(\mathrm{PtP})$ = 2 752 Hz is typical for mutually *trans*-bonded phosphorus donor atoms. Both complexes [$\overline{\mathrm{M(P{-}O}}\mathrm{)_2}$] (**3**; R = Ph) were too insoluble for n.m.r. studies but it seems extremely likely that they also have a *trans* configuration. All the complexes of type (**3**) showed one or two strong bands at *ca.* 1 500 cm$^{-1}$ due to $\nu$(C=C) + $\nu$(C–O) (see Table 3). Carty *et al.*[7] found bands for [$\overline{\mathrm{PdCl\{Ph_2PCH{=}C(O}}\mathrm{)CF_3\}}$-{$\mathrm{PPh_2(OEt)}$}] at somewhat higher wavenumbers, *viz.* 1 569 and 1 581 cm$^{-1}$, and these were also assigned to $\nu$(C=C) + $\nu$(C–O).



(**3**)

## EXPERIMENTAL

The general techniques and apparatus used were the same as in other recent papers from this laboratory.[10]

*Phenacyldi-t-butylphosphonium Bromide.*—Di-t-butylphosphine (6.5 g, 45 mmol) was added dropwise to phenacyl bromide (8.8 g, 45 mmol) in acetone (20 cm$^3$) with stirring over a period of 5 min. The mixture was stirred for another 10 min and cooled to 5 °C. The product was filtered off as white microcrystals. Yield 10.3 g, 30 mmol, 67%.

Pivaloylmethyldi-t-butylphosphonium bromide was made similarly as white hygroscopic *needles* which were used immediately, and without characterization, for the preparation of the free phosphine.

*Phenacyldi-t-butylphosphine.*—A solution of sodium acetate (4 g, 49 mmol) in degassed water (20 cm$^3$) was added to a solution of the phosphonium salt (5.2 g, 15 mmol) in degassed water. The phosphine was isolated with diethyl ether and distilled as a colourless liquid (3.7 g, 14 mmol, 93%), b.p. 130—135 °C (0.005 mmHg).*

Pivaloylmethyldi-t-butylphosphine was prepared similarly. Yield 60%, b.p. 110—115 °C (0.01 mmHg).

[$\overline{\mathrm{Ni\{Bu^t_2PCH{=}C(O}}\mathrm{)Ph\}_2}$].—The ketophosphine (0.45 g, 1.69 mmol) was added to a solution of nickel(II) chloride hexahydrate (0.20 g, 0.84 mmol) in ethanol (*ca.* 10 cm$^3$). The required product separated as a mustard-yellow precipitate which formed yellow needles, subliming at >300 °C, from pyridine. Yield 0.31 g, 0.52 mmol, 62%.

The complex [$\overline{\mathrm{Ni\{Bu^t_2PCH{=}C(O}}\mathrm{)Bu^t\}_2}$] was made similarly and formed orange-yellow needles, m.p. 250 °C with sublimation, from ethanol. Yield 28%.

*trans*-[$\mathrm{PdCl_2\{PBu^t_2(CH_2COPh)\}_2}$].—The ketophosphine (0.44 g, 1.7 mmol) was added to a suspension of bis(benzonitrile)dichloropalladium(II) (0.32 g, 0.84 mmol) in ethanol (*ca.* 15 cm$^3$). The mixture was heated under reflux for *ca.* 30 min and cooled giving the required compound as yellow prisms, m.p. 195—205 °C. Yield 0.24 g, 0.38 mmol, 74%.

The following complexes were prepared similarly: *trans*-[$\mathrm{PdCl_2\{PBu^t_2(CH_2COBu^t)\}_2}$], yellow prisms, m.p. 168—190 °C (decomp.), yield 83%; *trans*-[$\mathrm{PtCl_2\{PBu^t_2(CH_2COPh)\}_2}$], pale yellow prisms, m.p. 310 °C with sublimation, yield 81%; and *trans*-[$\mathrm{PtCl_2\{PBu^t_2(CH_2COBu^t)\}_2}$], yellow prisms, m.p. 185—190 °C with sublimation, yield 91%.

[$\overline{\mathrm{Pd\{Bu^t_2PCH{=}C(O}}\mathrm{)Ph\}_2}$].—A solution of sodium 2-methoxyethoxide (1.3 mmol) in 2-methoxyethanol (0.6 cm$^3$) was added to a suspension of *trans*-[$\mathrm{PdCl_2\{PBu^t_2(CH_2COPh)\}_2}$] (0.37 g, 0.52 mmol) in 2-methoxyethanol (10 cm$^3$). The mixture was heated under reflux for *ca.* 30 min and cooled, giving the required product as yellow prisms (0.24 g, 0.38 mmol, 74%) which melted at *ca.* 250 °C with sublimation.

The following complexes were prepared similarly from the corresponding dichlorides: [$\overline{\mathrm{Pd\{Bu^t_2PCH{=}C(O}}\mathrm{)Bu^t\}_2}$], yellow prisms, m.p. 258—259 °C with sublimation, yield 98%; [$\overline{\mathrm{Pt\{Bu^t_2PCH{=}C(O}}\mathrm{)Ph\}_2}$], yellow microcrystals, m.p. 310 °C with sublimation, yield 81%; [$\overline{\mathrm{Pt\{Bu^t_2PCH{=}C(O}}\mathrm{)Bu^t\}_2}$], yellow microcrystals, m.p. 185—190 °C with sublimation, yield 91%.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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