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Preliminary communication

BIDENTATE PHOSPHINES, $(PPh_2)_2NCHRCO_2Me$ (R = H, OR, i-Pr), DERIVED FROM α-AMINO-ACID ESTERS, AND TRANSITION METAL COMPLEXES THEREOF

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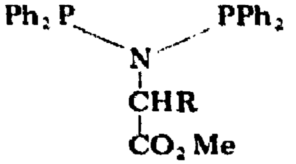
Summary

Reaction of Ph_2PCl with NH_2CHRCO_2Me (R = H, i-Pr) affords stable bidentate aminophosphines, $(Ph_2P)_2NCHRCO_2Me$; transition metal complexes (optically active for R = i-Pr) are reported for molybdenum(0), rhodium(I) and palladium(II).

Optically active bidentate phosphines have recently been used as ligands in transition metal catalysed asymmetric induction [1]. We now report a novel type of bidentate phosphine, I, easily synthesized from the readily available α-amino-acid esters GlyOMe or L—ValOMe. These phosphines are white, crystalline, monomeric, air and moisture stable compounds, forming transition metal complexes which are optically active for R = i-Pr.



(I) R = H, i-Pr

The phosphines (R = H, m.p. 120°C; R = i-Pr; m.p. 182—183°C) are prepared in 40—50% yield by the anaerobic reaction ($CHCl_3$, overnight, ambient temperature) of Ph_2PCl (2 mol) with $Cl\ {}^{+}NH_3CHRCO_2Me$ (1 mol) and Et_3N (3 mol). Chelated transition metal complexes of the phosphines

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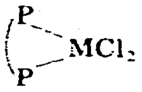
[(PP) = (Ph$_2$P)$_2$NCHRCO$_2$Me], II—VI, are formed by displacement of labile ligands.

(II)

R = H, M = Cr, Mo, W;
R = i-Pr, M = Mo; from [M(CO)$_6$]+$h\nu$
or from [M(CO)$_4$(norbornadiene)]

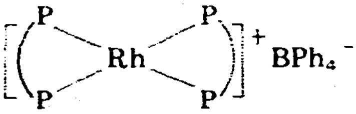
(III)

R = H
from [W(CO)$_5$THF]



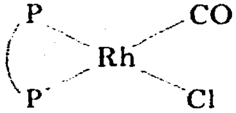
(IV)

R = H, M = Pd, Pt;
R = i-Pr, M = Pd;
from [MCl$_2$(NCPh)$_2$]



(V)

R = H, i-Pr
from [RhCl(1,5-COD)]$_2$



(VI)

R = i-Pr
from [RhCl(CO)$_2$]$_2$

Ligand vibrations are: II: ν(CO), cyclohexane, R = H, M = Cr, 2013, 1931, 1907 cm^{-1}; R = H, M = Mo, 2026, 1936, 1918, 1914 cm^{-1}; R = H, M = W, 2022, 1929, 1908 cm^{-1}; R = i-Pr, M = Mo, 2024, 1938, 1910, 1902 cm^{-1}. III: ν(CO), cyclohexane 2073, 1987, 1948, 1933 cm^{-1}. IV: ν(M—Cl), KBr: R = H, M = Pd, 298, 282 cm^{-1}; R = H, M = Pt, 308, 290 cm^{-1}; R = i-Pr, M = Pd, 302, 285 cm^{-1}. VI: ν(CO), CH$_2$Cl$_2$, 2015 cm^{-1}, ν(M—Cl), KBr, 298 cm^{-1}.

Selected physical data* are presented in Table 1. Analogous compounds of Mo and Pd with EtN(PPh$_2$)$_2$ have been reported [2].

The ^{1}H NMR spectrum (CDCl$_3$, 60 MHz) of (Ph$_2$P)$_2$NCH$_2$CO$_2$Me shows coupling of the methylene protons to 2 equivalent P atoms (τ (ppm) 2.70,

TABLE 1

$[\alpha]^{578}_{20}$ AND NMR DATA FOR SOME OF THE COMPOUNDS OBTAINED

Compound [a]	$[\alpha]^{578}_{20}$ [b]	NMR data for isopropyl methyl groups [c] τ (ppm); J(Hz)
(PP)	−77°	9.12; 7.5 [d]
[Mo(CO)$_4$(PP)]	+99°	9.75 doublet; 6.5 10.22 doublet; 6.5
[PdCl$_2$(PP)]	−32°	9.63 doublet; 6.5 10.40 doublet; 6.5
[{Rh(PP)$_2$}BPh$_4$]	+30°	9.75 doublet; 6.5 10.63 doublet; 6.5

[a] (PP) = (PPh$_2$)$_2$NCH-i-PrCO$_2$Me. [b] CHCl$_3$, c 15—80 mg ml^{-1}. [c] 60 MHz, CDCl$_3$, TMS. [d] Apparent triplet.

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* Satisfactory analytical and spectroscopic data have been obtained for all compounds.

s, 20 H; 5.97, t, (J 11 Hz), 2H; 6.70, s, 3H). On complexation the methylene and methyl resonances are shifted 0.3—0.5 ppm upfield; for the Rh complex V(R = H) ^3J(PNCH) decreases to 6 Hz. The isopropyl methyl groups of $(Ph_2P)_2NCH\text{-}i\text{-}PrCO_2Me$ are diastereotopic, resonating at 60 MHz as an apparent triplet, formed from two overlapping doublets. In the transition metal complexes the doublets are well separated, and one occurs to high field of TMS (see Table 1).

A similar, although much smaller, separation of the valine isopropyl methyl doublets was observed in the compounds $R'C(Cl)HCONHC\text{-}i\text{-}PrHCO_2Me$ [3]. The separation increased with the size of R′; our compounds would appear to follow this trend.

Potential applications of the compounds described are (a) in catalysis, with the possibility of asymmetric induction when R = H, (b) in peptide synthesis, as *N*-protected α-amino-acid derivatives (cf. the use of Cr [4] or Pt [5] compounds) and (c) in reactions of I (R = H) at the methylene group. We are currently investigating each of these areas, and preliminary results show that (a) compound VI is a hydrogenation or hydroformylation catalyst, (b) the P—N bond in I (R = H) is rapidly and quantitatively cleaved by HCl to yield $Cl^-\ ^+NH_3CH_2CO_2Me$, (c) mono-alkylation of I (R = H) with $PnCH_2Br$/t-BuOK gives the corresponding phenylalanine derivative $(Ph_2P)_2NC(CH_2Ph)HCO_2Me$.

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