Complexes of Platinum, Palladium, and Rhodium with Tertiary Phosphine Carboxylic Esters and Carboxylic Acids †

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The new tertiary phosphine esters $Bu^t_2P(CH_2)_nCO_2Et$ [L^1(n = 1), L^2(n = 2), and L^3(n = 3)] are described. Treatment of *trans*-[$PtCl_2L^1_2$] with NaI in refluxing ethanol gives the *O*-metallated species [$PtI(OCOCH_2PBu^t_2)L^1$], which on heating with Na[O_2CMe] in 2-methoxyethanol give *trans*-[$Pt(OCOCH_2PBu^t_2)_2$]. The ^1H and ^{31}P n.m.r. spectra of [$PtI(OCOCH_2PBu^t_2)L^1$] vary with temperature due to the presence of two rotamers, and the complex is reduced by Na[BH_4] to [$PtH(OCOCH_2PBu^t_2)(Bu^t_2PCH_2CH_2OH)$]. With hydrazine, *trans*-[$PtCl_2L^1_2$] gives the very stable [$PtCl(Bu^t_2PCH_2CONNHCOCH_2PBu^t_2)$] containing a tridentate ligand. The complex [$PtCl_2(NCBu^t)_2$] with L^2 (1 mol proportion) gives the binuclear [$Pt_2Cl_4L^2_2$]; similarly with L^3 [$Pt_2Cl_4L^3_2$] is formed which when heated in toluene undergoes *C*-metallation to give [$Pt_2Cl_2(Bu^t_2PCH_2CH_2CHCO_2Et)_2$] (mixtures of isomers) which in turn with PPh_3 gives [$PtCl(Bu^t_2PCH_2CH_2CHCO_2Et)(PPh_3)$] (single isomer). Attempts to effect *O*-metallation with [$PdCl_2L^1_2$] lead to decomposition, but with ammonia the bischelate [$Pd(NHCOCH_2PBu^t_2)_2$] isfor med. Binuclear species [$Pd_2X_4L^2_2$] (X = Cl or I) have been prepared, and also *cis*-[$PtCl_2Q_2$] and *trans*-[$PdCl_2Q_2$] (Q = $Ph_2PCH_2CO_2Et$). These $Ph_2PCH_2CO_2Et$ complexes do not undergo *O*-metallation when heated with NaI, the complexes *trans*-[MI_2Q_2] being formed. However, treatment of [$PdCl_2(NCPh)_2$] with $Ph_2PCH_2CO_2H$ gives [$PdCl(OCOCH_2PPh_2)(Ph_2PCH_2CO_2H)$] which with Na[$O_2CMe$] gives [$Pd(OCOCH_2PPh_2)_2$]; similarly for platinum. The compound $RhCl_3{\cdot}3H_2O$ reacts with L^1 to give the six-co-ordinate rhodium(III) species [$RhCl_2(Bu^t_2PCH_2COOEt)_2$]$^+$ isolated as its tetraphenylborate salt. This cation is converted by Na[BH_4] to [$RhH_2(BH_4)(Bu^t_2PCH_2CO_2Et)_2$]. The compound $RhCl_3{\cdot}3H_2O$ reacts with L^2 or L^3 to give the rhodium(II) species *trans*-[$RhCl_2L^2_2$] or *trans*-[$RhCl_2L^3_2$], respectively.

IT has been shown that one or two bulky t-butyl groups on tertiary phosphine ligands often generate unusual chemistry in the complexes which they form with transition metals.[1-8] In most cases the other organic radicals attached to the phosphorus have been hydrocarbon but (2-methoxyphenyl)di-t-butylphosphine also generates unusual chemistry.[4] In general, however, there have been few studies of tertiary phosphine ligands containing functional groups. It was therefore of interest to study bulky tertiary phosphines containing an ester function and we chose to study the series $Bu^t_2P[CH_2]_nCO_2Et$ (n = 1—3) in which the ester group is situated at an increasing distance from the phosphorus-donor atom. We anticipated that the ester group might undergo *O*-metallation or activate an adjacent methylene group towards *C*-metallation. In addition we expected that the ester group could be converted into other functional groups by treatment with suitable reagents.

RESULTS AND DISCUSSION

We prepared the phosphines by treating di-t-butylphosphine with the appropriate bromo-ester in acetone or ethyl methyl ketone and subsequent treatment of the phosphonium salt with sodium acetate. The phosphines were isolated by distillation. The ester $Bu^t_2PCH_2CO_2Et$ was characterized by conversion into its methiodide salt. Details of preparations are given in the Experimental section. For comparison we also prepared some complexes from the known and much less bulky phosphines $Ph_2PCH_2CO_2Et$ and $Ph_2PCH_2CO_2H$.[9] The former phosphine readily gave the solid hydrazide $Ph_2PCH_2CONHNH_2$ when treated with hydrazine hydrate and this in turn was acetylated with acetyl chloride to give $Ph_2PCH_2CONHNHCOMe$ and treated with acetone to give $Ph_2PCH_2CONHNCMe_2$. These crystalline nitrogen-containing phosphines give complexes with platinum(II) or or palladium(II) halides but we have not studied these products in any detail and do not report on them here.

We have studied some complexes of the ligands $Bu^t_2P[CH_2]_nCO_2Et$ (n = 1—3) with Pt^{II} and to a lesser extent Pd^{II}, Rh^{III}, and Rh^{II}. Treatment of *trans*-[$MCl_2(NCPh)_2$] (M = Pt or Pd) with 2 mol equiv. of $Bu^t_2PCH_2CO_2Et$ (L^1) in dichloromethane gave *trans*-[$MCl_2L^1_2$] (see Experimental section and Tables 1 and 2). An attempt to prepare [$PtI_2L^1_2$] by a metathesis reaction, *i.e.* by treatment of *trans*-[$PtCl_2L^1_2$] with sodium iodide in acetone, gave a mixture of an orange solid (possibly the required iodide) and a yellow solid. This yellow solid was formed in good yield by treating *trans*-[$PtCl_2L^1_2$] with NaI in boiling ethanol for 5 h. Analytical and spectroscopic studies show this complex to be [$PtI(OCOCH_2PBu^t_2)L^1$], *i.e.* *O*-metallation has occurred

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† No reprints available.

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TABLE 1

Microanalytical,[a] molecular-weight,[a] ^{1}H n.m.r.,[b] and i.r. data. $L^1 = Bu^t_2PCH_2CO_2Et$, $L^2 = Bu^t_2P(CH_2)_2CO_2Et$, $L^3 = Bu^t_2P(CH_2)_3CO_2Et$, and $Q = Ph_2PCH_2CO_2Et$

	Microanalysis (%)					^{1}H N.m.r. data					I.r. (cm^{-1}) (Nujol)	
	C	H	Halogen	N	M	$\delta(Bu^t)$	J(PH)	$\delta(PCH_2)$	J(PH)	J(PtH)	ν(M–Cl)	ν(CO)
$[PdCl_2L^1_2]$	44.9 (44.9)	7.7 (7.9)	10.9 (11.1)			1.54 (t)	14.0[c]	3.24 (t)	6.6[d]	26.5	345s	1 735vs
$[PtCl_2L^1_2]$	39.6 (39.5)	6.9 (6.9)	9.9 (9.7)			1.54 (t)	14.0[c]	3.22 (t)	6.5[d]		330s	1 730vs
$[PdCl_2L^2_2]$	46.8 (46.6)	8.0 (8.1)	10.4 (10.6)			1.50 (t)	13.5[c]	2.25 (m) 2.79 (m)			342s	1 720vs
$[PdCl_2L^3_2]$	48.5 (48.4)	8.3 (8.3)	10.3 (10.2)			1.48 (t)	13.3[c]	2.00 (m) 2.41 (m)			354s	1 732vs
$[PtCl_2L^2_2]$	41.0 (41.2)	7.1 (7.2)	9.5 (9.4)			1.52 (t)	13.0[c]	2.20 (m) 2.63 (m)			338s	1 730vs
$[PtCl_2L^3_2]$	43.0 (42.7)	7.4 (7.4)	9.2 (9.0)			1.50 (t)	12.8[c]	2.05 (m) 2.40 (m)			342s	1 730vs
$[PdCl_2Q_2]$	53.3 (53.2)	4.7 (4.8)	9.7 (9.8)					3.68 (t)	8.4[d]		348s	1 720vs
$[PtCl_2Q_2]$	47.9 (47.4)	8.5 (8.8)	4.3 (4.2)					3.62 (d)	10.8		317s 291s	1 729vs 1 715vs
$[PdI_2Q_2]$	42.0 (42.5)	3.7 (3.8)	27.1 (28.1)					3.19 (t)	7.2[d]			
$[PtI_2Q_2]$	39.4 (38.7)	3.6 (3.5)	25.3 (25.6)					3.14 (t)	9.0[d]			1 718vs
$[Pd_2I_4L^2_2]$	26.2 (25.7)	4.6 (4.5)	41.8 (41.9)			1.52 (d)	14.2					1 725vs
$[Pd_2I_4L^3_2]$	27.6 (27.1)	4.6 (4.7)	40.8 (40.9)			1.53 (d)	14.2					1 722vs
$[PtI(OCOCH_2PBu^t_2)L^1]$	35.0 (34.9)	6.0 (6.0)	17.0 (16.8)		750 (758)	*e*	*e*	*e*	*e*			
$[Pt(OCOCH_2PBu^t_2)_2]$	40.4 (40.4)	7.0 (6.7)			617 (602)	1.45 (t)	15.3[c]	2.52 (t)	7.5[d]	20.1		1 640vs
$[PtH(Bu^t_2PCH_2CO_2)\{Bu^t_2P(CH_2)_2OH\}]$	41.1 (40.8)	7.7 (7.6)				*f*	*f*	*f*	*f*			1 605s
$[Pd(NHCOCH_2PBu^t_2)_2]\cdot 0.1CH_2Cl_2$ [g]	46.2 (46.4)	8.2 (8.1)	1.3 (1.4)	5.4 (5.0)	508 (519)	1.38 (t)	14.5[c]	2.49 (t)	6.0			1 585
$[PtCl(Bu^t_2PCH_2CONNHCOCH_2PBu^t_2)]$ [h]	38.0 (37.9)	6.5 (6.5)	5.5 (5.6)	4.4 (4.3)		1.53 (d) 1.51 (d) 1 43 (d) 1.41 (d)	12.5 13.0 13.0 13.2	2.93 (d) 2.82 (d) 2.69 (d) 2.59 (d)	9.8 10.2 9.8 10.0	31.2 31.2 14.0 14.0	328s	1 660vs 1 610vs
$[Pd_2Cl_4L^2_2]\cdot 0.2CH_2Cl_2$	37.1 (36.7)	6.4 (6.4)	18.3 (18.2)			1.55 (d)	14.7	2.18 (m) 2.86 (m)			347s 198s	1 728vs
$[Pt_2Cl_4L^2_2]\cdot 0.3CH_2Cl_2$	30.4 (29.8)	5.2 (5.2)	16.6 (16.4)			1.61 (d)	14.3	2.14 (m)			346s 340 (sh) 323, 313w 263m	1 730vs
$[Pd_2Cl_4L^3_2]$	38.6 (38.4)	6.7 (6.7)	16.2 (16.2)			1.66 (d)	14.5	2.09 (m) 2.43 (m)			355s 298m 259m	1 720vs
$[Pt_2Cl_4L^3_2]$	32.4 (32.0)	5.6 (5.6)	13.4 (13.5)								352s 315m 264m	1 730vs
$[Pt_2Cl_2\{Bu^t_2P(CH_2)_2CHCO_2Et\}_2]$	34.7 (34.3)	5.7 (5.8)	7.4 (7.3)		1 002 (980)	1.37 (d)	14.2				287ms 250m	1 705s (sh) 1 685s
$[PtCl_2\{Bu^t_2P(CH_2)_2CHCO_2Et\}(PPh_3)]$	51.3 (51.1)	5.8 (5.8)	5.1 (4.7)			1 46 (d) 1.49 (d)	13.9 12.7	1.95 (m) 2.50 (m)			279m	1 689s
$[PdCl(OCOCH_2PPh_2)(Ph_2PCH_2CO_2H)]$	52.7 (53.4)	4.2 (4.0)	5.4 (5.6)					3.79 (d)[i]	11.4[i]		302m	1 718s 1 602vs
$[PtCl(OCOCH_2PPh_2)(Ph_2PCH_2CO_2H)]$	46.4 (46.8)	5.0 (4.9)	3.5 (3.5)					3.61 (d)[i] 3.81 (d)[i]	12.0[i] 12.0[i]		312s	1 722s 1 610vs
$[Pd(OCOCH_2PPh_2)_2]$	56.8 (56.7)	4.3 (4.1)				*j*						1 635vs
$[Pt(OCOCH_2PPh_2)_2]$	49.8 (49.3)	3.6 (3.6)				*j*						1 650vs
$[PdCl_2\{Bu^t_2P(CH_2)_3CO_2H\}_2]$	44.9 (44.9)	7.9 (7.9)	11.3 (11.1)			*j*					348s	1 712s

TABLE 1 (*Continued*)

	Microanalysis (%)					^{1}H N.m.r. data					I.r. (cm^{-1})(Nujol)	
	C	H	Halogen	N	*M*	δ(Bu^t)	*J*(PH)	δ(PCH$_2$)	*J*(PH)	*J*(PtH)	ν(M–Cl)	ν(CO)
$[PtCl_2\{Bu^t_2P(CH_2)_3CO_2H\}_2]$	40.4 (39.5)	6.9 (6.9)	9.5 (9.7)			[j]					327m	1 712vs
$[RhClL^1_2][BPh_4]$	60.0 (60.2)	7.7 (7.4)	7.8 (7.4)	1.3 (1.2)		1.30 (t) [c] 1.53 (t) [c]	13.9 15.1	3.29 (m)			350s	1 598s 1 581vs
$[RhH_2(BH_4)L^1_2]$ [k]	50.1 (49.4)	9.9 (9.7)		1.8 (1.9)	574 (584)	1.53 (t) [c]	13.5	3.32 (t)	6.0			1 738s 1 718s 1 710s
$[RhCl_2L^2_2]$	47.2 (46.9)	8.1 (8.2)	10.4 (10.6)								352s	1 730vs
$[RhCl_2L^3_2]$	48.1 (48.5)	8.4 (8.4)	10.4 (10.2)								358s	1 730v

[a] Calculated values are given in parentheses. [b] At 60 MHz in $CDCl_3$, unless stated otherwise. δ ±0.02 p.p.m., *J* ±0.2 Hz. All the ethoxycarbonyl compounds showed the resonance patterns of an ethyl group but these data are not reported. [c] ^3J(PH) + ^5J(PH). [d] ^2J(PH) + ^4J(PH). [e] Complex and temperature dependent, see text. [f] See text. [g] δ(NH) or δ(OH) 4.67 (br), δ(CH_2Cl_2) 5.30 p.p.m. [h] δ(NH) 8.75 (br), ^2J(PtH) 30.2 Hz. [i] In dimethyl sulphoxide. [j] Insoluble. [k] δ(RhH) −18.5 (dt, br) p.p.m., ^2J(PH) 15.5, ^1J(RhH) 15.5 Hz.

with loss of an ethyl group. The ^{1}H and ^{31}P n.m.r. spectra of this complex vary with temperature, and we attribute this to the presence of two rotamers (1a) and (1b). Thus at **233** K in $CDCl_3$ the ^{31}P spectrum consists of two AB patterns with satellites due to platinum-195 splitting (Table 2). The ratio of the two species is *ca.* 1 : 1.7. At **323** K the spectrum consists of only one AB pattern whilst at *ca.* 300 K broad resonances are observed. The large values of ^2J(PP) (Table 2) are clearly indicative of *trans*-phosphorus-donor atoms. The ^{1}H n.m.r. patterns similarly show the presence of two species at low (244 K) and apparently one species at higher (345 K) temperature. The i.r. spectrum shows two sets of strong bands due to ν(CO) at 1 730 and 1 740 and at 1 643 and 1 668 cm^{-1}, presumably due to the two rotamers.

TABLE 2

Phosphorus-31 n.m.r. data * for some platinum complexes of $Bu^t_2PCH_2CO_2Et$ (L^1) and $Bu^t_2PCH_2CH_2\dot{C}HCO_2Et$

Complex	Conditions, *T*/K (solvent)		δ	^2J(PP)	^1J(PtP)
$[PtI(OCOCH_2PBu^t_2)L^1]$	233 ($CDCl_3$)	(1a) or (1b)	19.81 36.34	391	2 294 1 569
		(1b) or (1a)	24.98 34.93	393	2 272 2 612
	323 ($CDCl_3$)		20.98 35.98	399	2 321 2 618
$[PtH(OCOCH_2PBu^t_2)L^1]$	293 (C_6D_6)		58.81 58.84	342	1 806 2 717
$[PtCl(Bu^t_2PCH_2CONNHCOCH_2PBu^t_2)]$	293 (C_6D_6)		17.93 65.15	395	1 686 2 348
$[Pt_2Cl_2(Bu^t_2PCH_2CH_2CHCO_2Et)_2]$	300		79.75 79.89 80.02		*ca.* 4 750 *ca.* 4 750 *ca.* 4 750
$[PtCl(Bu^t_2PCH_2CH_2CHCO_2Et)(PPh_3)]$	300		27.58 79.58	413	3 191 2 818

* *J* ±0.4 Hz, δ ±0.02 p.p.m.

When the complex $[PtI(OCOCH_2PBu^t_2)L^1]$ was treated with sodium tetrahydroborate, reduction to $[PtH(OCOCH_2PBu^t_2)(Bu^t_2PCH_2CH_2OH)]$ (2) occurred. This complex shows bands due to ν(CO) (1 605 cm^{-1}), ν(PtH) (2 242 cm^{-1}), and ν(OH) (3 240 and 3 440 cm^{-1}) in its i.r. spectrum. The ^{31}P n.m.r. spectrum consists of one AB pattern with ^{195}Pt sidebands and ^2J(PP) 342 Hz, and does not vary with temperature in contrast with $[PtI(OCOCH_2PBu^t_2)(Bu^t_2PCH_2CO_2Et)]$ as described above. This is probably due to less-hindered rotation around the Pt–P bond caused by replacement of iodide by the smaller hydride ligand. The 60-MHz ^{1}H n.m.r. spectrum of the complex in $CDCl_3$ shows an apparent triplet at δ 1.30 p.p.m. due to the t-butyl protons, but at 90 MHz in C_6D_6 this changes to two second-order triplets at δ 1.02 [$|^3J(PH) + {}^5J(PH)|$ 14.4] and 1.15 p.p.m. [$|^3J(PH) + {}^5J(PH)|$ 13.4 Hz]. The second-order nature arises because $|^2J(PP)| > \Delta(PP)$ (the difference in chemical shift).[10-12] Similarly the low-field satellite (due to ^{195}Pt coupling) of the hydride resonance at δ −12.05 p.p.m. shows considerable second-order character (the low-field ^{195}Pt satellite in the ^{31}P spectrum at 36.43 MHz is an apparent singlet). The n.m.r. data are in the Tables.

Prolonged (24-h) treatment of *trans*-$[PtCl_2L^1_2]$ with

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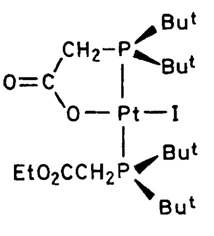
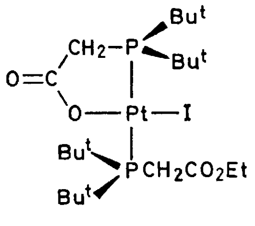
NaI in boiling 2-methoxyethanol gave only $[\mathrm{PtI(OCOCH_2PBu^t{}_2)L^1}]$, *i.e.* further metallation did not occur. However, we have shown that metallation can be promoted by sodium acetate [13] and similar treatment by $\mathrm{Na[O_2CMe]}$ gave *trans*-$[\mathrm{Pt(OCOCH_2PBu^t{}_2)_2}]$ in 77% yield (see Tables for characterizing data). The sodium acetate could promote base cleavage of the ethoxy-group of the phosphine ligand or reaction might proceed *via* $[\mathrm{Pt(O_2CMe)_2L^1{}_2}]$, as suggested for the *C*-metallation of (1-naphthyl)phosphines.[14]

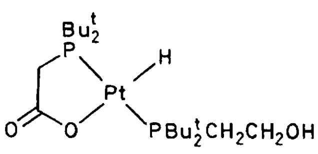


(1a)

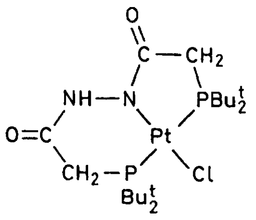


(1b)

Ethyl esters of carboxylic acids react with hydrazine or ammonia to give hydrazides or amides respectively. When *trans*-$[\mathrm{PtCl_2L^1{}_2}]$ was boiled in ethanol containing hydrazine hydrate for 10 min the solution became pale yellow. The solution was evaporated to dryness and the bulk of the residue was very soluble in water to give a colourless solution. We could not isolate pure material from the aqueous solution (even on adding large cations). However, the remaining residue was extracted into dichloromethane and isolated as very stable yellow prisms. These could be sublimed at 240 °C (0.05 mmHg) * with no decomposition. The analytical and spectral data (Tables) fit the formulation $[\mathrm{PtCl(Bu^t{}_2PCH_2CONNHCOCH_2PBu^t{}_2)}]$ (3) containing a tridentate ligand. The i.r. spectrum shows bands at 328vs $\mathrm{cm^{-1}}$ [ν(PtCl)], 1 660s and 1 610s $\mathrm{cm^{-1}}$ [ν(CO)], and 3 330m, 3 175m, and 3 100m $\mathrm{cm^{-1}}$ [ν(NH)]. At 60 or 90 MHz the ^{1}H n.m.r. pattern for the t-butyl groups consists of four doublets and at 90 MHz each of the four $\mathrm{PC}H_2$ protons gives a doublet with platinum satellites. A broad signal at δ 8.75 p.p.m. with platinum satellites is assigned to the NH proton. The ^{31}P n.m.r. spectrum shows that the phosphorus nuclei are mutually *trans*, ^2J(PP) 395 Hz (Table 2). A possible route to (3) involves the intermediate formation of $[\mathrm{PtCl(Bu^t{}_2PCH_2CONNH_2)(Bu^t{}_2PCH_2CO_2Et)}]$ followed by attack of the $\mathrm{NH_2}$ group on the adjacent ethoxycarbonyl group and elimination of ethanol.

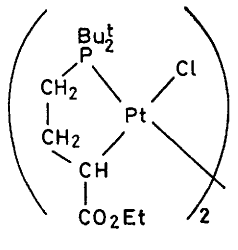


(2)

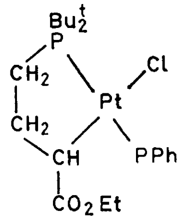


(3)

The homologous phosphines, $\mathrm{Bu^t{}_2P[CH_2]_{\mathit{n}}CO_2Et}$ [n = 2 ($\mathrm{L^2}$) or 3 ($\mathrm{L^3}$)] reacted with $[\mathrm{PtCl_2(NCBu^t)_2}]$ (2 : 1 ratio of ligand to metal) in dichloromethane to give yellow complexes of type *trans*-$[\mathrm{PtCl_2L^2{}_2}]$ or *trans*-$[\mathrm{PtCl_2L^3{}_2}]$. These dichloro-complexes were recovered unchanged after being boiled with NaI in refluxing ethanol for up to 24 h. When $[\mathrm{PtCl_2(NCBu^t)_2}]$ was treated with $\mathrm{L^2}$ or $\mathrm{L^3}$ (1 : 1 ligand : metal) in refluxing toluene for *ca.* 1 min the binuclear species $[\mathrm{Pt_2Cl_4L^2{}_2}]$ or $[\mathrm{Pt_2Cl_4L^3{}_2}]$ were formed. Further refluxing of $[\mathrm{Pt_2Cl_4(Bu^t{}_2PCH_2CH_2CH_2CO_2Et)_2}]$ in toluene for 3.5 h gave hydrogen chloride and an internally metallated prouct whose structure we suggest is $[\mathrm{Pt_2Cl_2(Bu^t{}_2PCH_2CH_2CHCO_2Et)_2}]$ (4). This formulation is based on microanalytical, i.r., and n.m.r. data (Tables). In particular the CO stretching frequency falls markedly to 1 685 from 1 730 $\mathrm{cm^{-1}}$ for $[\mathrm{Pt_2Cl_4L^3{}_2}]$, indicating that it is very likely that the carbon atom adjacent to the carbonyl group is the one that is metallated as shown in (4). The ^{31}P n.m.r. spectrum shows that the product in solution is a mixture of three very similar species. The complexes could have phosphines in overall *cis* or *trans* positions and for both of these there could be *dl* and *meso* forms since *C*-metallation generates an asymmetric centre. We could not prepare a mononuclear pentane-2,4-dionate (pd) derivative by treatment with Tl(pd) possibly because this reagent attacks the ester group. However, treatment of this three-component mixture of isomers with 1 mol equiv. of triphenylphosphine in dichloromethane gave a single white mononuclear species formulated as $[\mathrm{PtCl\{Bu^t{}_2PCH_2CH_2CHCO_2Et\}(PPh_3)}]$ (5) having *trans*-phosphorus nuclei [J(PP) 413 Hz, Table 2]. The ^{31}P n.m.r. spectrum (Table 2) shows only one species to be present. The i.r. spectrum has ν(PtCl) at 279 $\mathrm{cm^{-1}}$, a value typical for chlorine *trans* to carbon and the value of ν(CO) (1 689 $\mathrm{cm^{-1}}$) is little changed from the parent species.



(4)



(5)

We could find no evidence for *C*- or *O*-metallation in $[\mathrm{Pt_2Cl_4(Bu^t{}_2PCH_2CH_2CO_2Et)_2}]$, which was recovered unchanged even after heating under reflux in toluene for 3 h. For this complex *C*- or *O*-metallation would re-

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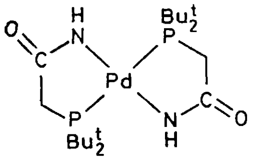
* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[13] J. M. Duff and B. L. Shaw, *J.C.S. Dalton*, 1972, 2219.

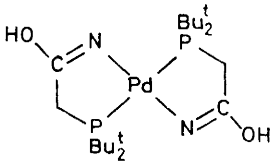
[14] J. M. Duff, B. E. Mann, B. L. Shaw, and B. L. Turtle, *J.C.S. Dalton*, 1974, 139.

quire the formation of four- or six-membered rings respectively.

We have made a less complete study of the corresponding *palladium* complexes, *trans*-$[PdCl_2\{Bu^t{}_2P(CH_2)_nCO_2Et\}_2]$, prepared in an analogous manner to the platinum complexes. The complex with $n = 1$, when treated with NaI, $Na[O_2CMe]$, or hydrazine hydrate in boiling ethanol, gave palladium metal. However, when *trans*-$[PdCl_2L^1{}_2]$ was treated with concentrated aqueous ammonia solution in boiling ethanol the pale yellow complex *trans*-$[\overline{Pd(NHCOCH_2P}Bu^t{}_2)_2]$ was isolated. This complex was purified by recrystallization from dichloromethane–light petroleum, and was shown by its ^1H n.m.r. spectrum to contain 1 mol of dichloromethane. Even prolonged heating *in vacuo* (24 h, 124 °C, 0.01 mmHg) failed to remove all the dichloromethane. The *trans* configuration follows from the triplet signal due to the t-butyl protons in the ^1H n.m.r. pattern. A broad signal at δ 4.67 p.p.m. is probably due to either the NH or OH protons. A strong broad band in the i.r. spectrum at 3 280 cm^{-1} is assigned to ν(NH) or ν(OH) and a very strong broad band at 1 588 cm^{-1} to ν(CO) or ν(CN). We cannot therefore distinguish between the keto- and hydroxy-structures (6) and (7) respectively. Treatment of the homologues *trans*-$[PdCl_2\{Bu^t{}_2P(CH_2)_nCOEt\}_2]$ (n = 2 or 3) with NaI in boiling ethanol gave the binuclear species $[Pd_2I_4\{Bu^t{}_2P(CH_2)_nCO_2Et\}_2]$. The binuclear species $[Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nCO_2Et\}_2]$ (n = 2 or 3) were prepared by treating $[PdCl_2(NCPh)_2]$ with the appropriate phosphine (1 : 1 molar ratio) in dichloromethane.



(6)



(7)

We have also studied complexes of the much less bulky phosphine $Ph_2PCH_2CO_2Et$ (Q) with Pt^{II} or Pd^{II}. Treatment of $[PtCl_2(NCBu^t)_2]$ with this ligand (2 mol per Pt atom) gave *cis*-$[PtCl_2Q_2]$. The *cis* stereochemistry follows from the white colour, the occurrence of two Pt–Cl stretching frequencies in the i.r. spectrum (Table 1), and of a doublet for the CH_2 protons in the n.m.r. spectrum (Table 1). Treatment of $[PdCl_2(NCPh)_2]$ with this ligand gave yellow *trans*-$[PdCl_2Q_2]$, the stereochemistry for which follows from the i.r. and n.m.r. evidence (Table 1). Both these complexes were converted into the corresponding *trans*-di-iodides when treated with NaI in ethanol (see Table 1 for characterizing data). These iodides showed no evidence of attack by the metal on the ethoxycarbonyl group when heated in ethanol, *i.e.* no internal *O*-metallation. Thus the tendency of the ethoxycarbonyl group towards *O*-metallation exactly parallels the behaviour of the 2-methoxyphenyl group towards *O*-metallation, *i.e.* $PBu^t{}_2(C_6H_4OMe\text{-}2)$ undergoes *O*-metallation much more readily than does $PPh_2(C_6H_4OMe\text{-}2)$.[4] Similar steric and conformational effects probably control the tendency of ethoxycarbonyl and 2-methoxyphenyl groups to undergo *O*-metallation.

We were, however, able to prepare the required chelate complexes using the carboxylic acid $Ph_2PCH_2CO_2H$. Treatment of $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCBu^t)_2]$ with $Ph_2PCH_2CO_2H$ (2.2 mol per metal atom) gave good yields of the rather insoluble species $[\overline{MCl(OCOCH_2P}Ph_2)(Ph_2PCH_2CO_2H)]$. The far-i.r. spectra of these species show bands assignable to ν(M–Cl) at 302 (M = Pd) and 312 cm^{-1} (M = Pt), characteristic of a chloride *trans* to an oxygen donor rather than a phosphine. Their near-i.r. spectra have two bands in the CO-stretching region, characteristic of a CO_2H (1 712 cm^{-1}) and a co-ordinated CO_2 (1 605 cm^{-1}) group; and also bands which can be assigned to ν(OH). These complexes reacted readily with $Na[O_2CMe]$ to give the bischelated species $[\overline{M(OCOCH_2P}Ph_2)_2]$ [ν(CO) at 1 635 (M = Pd) or 1 650 cm^{-1} (M = Pt)]. Like their precursors, these species were too insoluble for n.m.r. measurements. We also treated $[MCl_2\{Bu^t{}_2P(CH_2)_3CO_2Et\}_2]$ with ethanolic K[OH] to give water-soluble products, whose aqueous solutions on acidification yielded $[MCl_2\{Bu^t{}_2P(CH_2)_3CO_2H\}_2]$. There was no evidence for the formation of chelate rings with such systems.

Rhodium Complexes.—Treatment of $RhCl_3\cdot3H_2O$ with $Bu^t{}_2PCH_2CO_2Et$ in 1 : 4 mol proportion gave the cationic species $[\overline{RhCl_2(Bu^t{}_2PCH_2CO}OEt)_2]^+$ which was isolated as a tetraphenylborate salt. Chelation *via* the CO oxygen to give a six-co-ordinate species follows from the low CO stretching frequency in the i.r. spectrum (Table 1) and *trans*-chloro-ligands are indicated by the single Rh–Cl stretching absorption (350 cm^{-1}) seen in the far-i.r. spectrum. The t-butyl groups on each phosphine are magnetically non-equivalent, since two triplet resonances are observed for the t-butyl protons in the ^1H n.m.r. spectrum. Presumably, therefore, the chelate rings are not planar.

The Rh–Cl groups, but not the ester function, are reduced by $Na[BH_4]$ to give the complex $[RhH_2(BH_4)(Bu^t{}_2PCH_2CO_2Et)_2]$. This is assigned a structure with *trans*-phosphine ligands and *cis*-hydrido-ligands *trans* to a bidentate tetrahydroborate ligand. This structure, based on analytical and spectroscopic data (Table 1), is completely analogous to complexes of the type $[MH_2(BH_4)(PBu^t{}_2R)_2]$ (M = Ir or Rh; R = Ph or Bu^t) described previously.[15]

Rhodium trichloride reacted with 4 equivalents of L^2 or L^3 to give good yields of the paramagnetic rhodium(II) species $[RhCl_2L^2{}_2]$ or $[RhCl_2L^3{}_2]$. Other bulky phosphines containing hydrocarbon groups, *e.g.* $PBu^t{}_2R$ (R = Me, Et, or Pr^n) or $P(C_6H_4Me\text{-}2)_3$, similarly give rhodium(II) complexes.[16,17]

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[15] H. D. Empsall, E. Mentzer, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 861.

[16] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.

[17] C. Masters and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3679.

EXPERIMENTAL

All the operations involving di-t-butylphosphines were carried out under argon. The analytical and spectroscopic data are recorded in the Tables.

Ethyl Di-t-butylphosphinoacetate (L^1).—To a solution of di-t-butylphosphine (14.4 g, 99 mmol) in acetone (100 cm^3) was added ethyl bromoacetate (17.1 g, 102 mmol) in acetone (50 cm^3) over 1 h and the resulting mixture was stirred for 17 h. The solvent was removed under reduced pressure and the residue was dissolved in water (100 cm^3). The solution was neutralized with sodium acetate (8.5 g, 104 mmol) in water (50 cm^3) and the organic layer was extracted with diethyl ether (2 × 100 cm^3). The *product* was obtained by fractional distillation of the ether layer, yield 12.8 g (56%), b.p. 73—76 °C (0.3 mmHg).

Ethyl 3-*Di-t-butylphosphinopropionate* (L^2) *and* 4-*Di-t-butylphosphinobutyrate* (L^3).—Di-t-butylphosphine was heated under reflux with an equivalent amount of the bromoester *in* ethyl methyl ketone (*ca.* 10 cm^3 for each 10 mmol of phosphine) for 24 h. The precipitated phosphonium salt was isolated and converted into the free phosphine by an analogous method to that given above: yield 59% (L^2), b.p. 90—100 °C (0.1 mmHg); yield 57% (L^3), b.p. 110—115 °C (0.05 mmHg).

trans-*Dichlorobis*(*ethyl di-t-butylphosphinoacetate*)*platinum*(II).—A solution of bis(benzonitrile)dichloroplatinum(II) (1.45 g, 3.02 mmol) in dichloromethane (20 cm^3) was treated with L^1 (1.47 g, 6.50 mmol) and the resulting mixture was stirred for 5 min at 20 °C. The solution was diluted with methanol to give the *product* (1.98 g, 90%) as yellow prisms, m.p. 158—162 °C.

trans-*Dichlorobis*(*ethyl di-t-butylphosphinoacetate*)*palladium*(II) was prepared similarly from bis(benzonitrile)dichloropalladium(II) as orange prisms from dichloromethane–methanol, yield 87%, m.p. 166—170 °C.

(*Di-t-butylphosphinoacetato*-OP)(*ethyl di-t-butylphosphinoacetate*)*iodoplatinum*(II) (1).—A solution of *trans*-[PtCl$_2$(Bu$^t{}_2$PCH$_2$CO$_2$Et)$_2$] (0.500 g, 0.684 mmol) in ethanol (10 cm^3) containing sodium iodide (1 g) was heated under reflux for 5 h. The resulting yellow solution was evaporated to dryness and the residue was extracted with dichloromethane. The extract was diluted with n-heptane to give the *product* (0.418 g, 81%) as yellow prisms, m.p. 158—160 °C.

(*Di-t-butylphosphinoacetato*)(2-*di-t-butylphosphinoethanol*)*hydridoplatinum*(II) (2).—A solution of complex (1) (0.297 g, 0.406 mmol) in ethanol (10 cm^3) containing sodium tetrahydroborate (0.200 g) was boiled for 10 min during which time the yellow solution became colourless. The solution was evaporated to dryness and the residue was extracted with benzene and water. The benzene layer was diluted with n-heptane to give the product (0.131 g, 55%) as white prisms, m.p. 207—212 °C.

trans-*Bis*(*di-t-butylphosphinoacetato*-OP)*platinum*(II).— A mixture of *trans*-[PtCl$_2$(Bu$^t{}_2$PCH$_2$CO$_2$Et)$_2$] (0.500 g, 0.685 mmol) and sodium acetate trihydrate (0.47 g, 3.42 mmol) in 2-methoxyethanol (15 cm^3) was heated under reflux for 22 h. The resulting pale yellow solution was evaporated to dryness and the residue was extracted with dichloromethane and water. The dichloromethane layer was diluted with light petroleum (b.p. 60—80 °C) to give the *product* (0.317 g, 77%) as white prisms, m.p. 260 °C.

Action of Hydrazine Hydrate on trans-[PtCl$_2$(Bu$^t{}_2$PCH$_2$CO$_2$Et)$_2$].—A solution of the complex (1.00 g, 1.33 mmol) in ethanol (20 cm^3) containing hydrazine hydrate (1 cm^3) was heated under reflux for 25 min, when the yellow solution became paler. The solution was evaporated to dryness and the residue was extracted with dichloromethane and water. The organic layer was diluted with light petroleum (b.p. 60—80 °C) to give pale yellow prisms (0.177 g, 21%), m.p. 250 °C. These sublimed when heated to 240 °C (0.005 mmHg).

trans-*Bis*(*di-t-butylphosphinoacetamido*-NO)*palladium*(II)–*Dichloromethane*.—A solution of *trans*-bis(ethyl di-t-butylphosphinoacetate)palladium(II) (0.500 g, 0.780 mmol) in ethanol (10 cm^3) containing concentrated ammonia solution (1 cm^3) was boiled for 0.5 h when the initial orange solution had become pale yellow. The solution was evaporated to dryness and the residue was extracted with dichloromethane and water. The organic layer was diluted with light petroleum (b.p. 60—80 °C) to give the *product* (0.367 g, 81%) as pale yellow prisms, m.p. 303—305 °C.

Complexes trans-[MCl$_2${Bu$^t{}_2$P(CH$_2$)$_n$CO$_2$Et}$_2$] (M = Pd or Pt; n = 2 *or* 3).—Bis(benzonitrile)dichloropalladium(II) (0.383 g, 1 mmol) or dichlorobis(t-butyl cyanide)platinum(II) (0.432 g, 1 mmol) was dissolved in dichloromethane (5 cm^3) and the phosphine (2.2 mmol) was added. After a few minutes the solvent was removed by evaporation and the residue was dissolved in hot ethanol. The required product separated on cooling: Pd, L^2, yield 76%, m.p. 181—183 °C; Pt, L^2, yield 81%, m.p. 181—183 °C; Pd, L^3, yield 97%, m.p. 114—116 °C; Pt, L^3, yield 77%, m.p. 118—119 °C.

Ethyl diphenylphosphinoacetate was prepared by a modification of the method of Issleib and Thomas.[9] Lithium diphenylphosphide in tetrahydrofuran (thf) (0.1 mol in 200 cm^3) was added to a vigorously stirred solution of ethyl chloroacetate (0.1 mol) in thf (100 cm^3) at −78 °C over 30 min. The solvent was removed by rotary evaporation and the residue was shaken with benzene (200 cm^3), allowing removal of lithium chloride by filtration. The product was isolated by short-path high-vacuum distillation, b.p. 130—135 °C (0.05 mmHg), yield 72%.

Diphenylphosphinoacetohydrazide.—The above ester (1.3 g) was heated under reflux with hydrazine hydrate (1 cm^3) in methanol (10 cm^3) for 4 h. The product separated on cooling from benzene as white fibrous needles, m.p. 115 °C, yield 61% (Found: C, 65.1; H, 6.2. $C_{12}H_{15}N_2OP$ requires C, 65.9; H, 5.9%). When dissolved in hot acetone the *hydrazone* Ph$_2$PCH$_2$CONHNCMe$_2$ separated as white prisms, m.p. 138 °C, yield 69% (Found: C, 68.1; H, 6.7, $C_{15}H_{19}N_2OP$ requires C, 68.5; H, 6.4%). The *acetohydrazide*, Ph$_2$PCH$_2$CONHNHCOMe was prepared by dissolving the hydrazide (0.8 g) in acetyl chloride (3 cm^3) and pouring the resulting solution into cold water. It formed white prisms, m.p. 152 °C, yield 64% (Found: C, 63.7; H, 6.1. $C_{14}H_{17}N_2OP$ requires C, 63.6; H, 6.3%).

cis-*Dichlorobis*(*ethyl diphenylphosphinoacetate*)*platinum*(II).—The phosphine (0.530 g, 2.2 mmol) was added to a solution of dichlorobis(t-butyl cyanide)platinum(II) (0.432 g, 1 mmol) in dichloromethane (5 cm^3). The solvent was removed by evaporation and the residue was taken up in hot ethanol. The required product gradually separated, yield 0.470 g (58%), m.p. 203—204 °C. trans-*Dichlorobis*(*ethyl diphenylphosphinoacetate*)*palladium*(II) was prepared similarly, yield 75%, m.p. 119—121 °C.

trans-*Bis*(*ethyl diphenylphosphinoacetate*)*di-iodoplatinum*(II).—The corresponding dichloride (0.200 g, 0.246 mmol) was heated with NaI (0.6 g) in ethanol for a few minutes. The product separated from the solution on cooling as orange prisms (0.176 g, 0.177 mmol), yield 72%, m.p. 163—164 °C. trans-*Bis(ethyl diphenylphosphinoacetate)di-iodopalladium* was prepared similarly, yield 63%, m.p. 155—156 °C.

Di-μ-iodo-bis[*(ethyl 3-di-t-butylphosphinopropionate)iodopalladium*(II)].—A mixture of *trans*-$[\mathrm{PdCl_2(Bu^t{}_2PCH_2CH_2CO_2Et)_2}]$ (250 mg, 0.37 mmol) and NaI (500 mg, 3.3 mmol) was boiled in ethanol (8 cm^3) for 4 min. From the deep red solution, dark brown microcrystals of *product* precipitated on cooling, yield 35%, m.p. 236 °C (decomp.). *Di-μ-iodo-bis*[*(ethyl 4-di-t-butylphosphinobutyrate)iodopalladium*(II)] was prepared similarly, yield 36%, m.p. 224 °C (decomp.).

Di-μ-chloro-bis[*chloro(ethyl 3-di-t-butylphosphinopropionate)palladium*(II)].—The compound $\mathrm{Bu^t{}_2P(CH_2)_2CO_2Et}$ (0.246 g, 1 mmol) was added to a solution of $[\mathrm{PdCl_2(NCPh)_2}]$ (0.383 g, 1 mmol) in dichloromethane (5 cm^3). The solvent was removed under reduced pressure and the residue was dissolved in hot ethanol. Orange prisms of product precipitated from the cooled solution, yield 66%, m.p. 222—230 °C. *Di-μ-chloro-bis*[*chloro(ethyl 4-di-t-butylphosphinobutyrate)palladium*(II)] was prepared similarly, yield 55%, m.p. 182—184 °C.

Di-μ-chloro-bis[*chloro(ethyl 3-di-t-butylphosphinopropionate)platinum*(II)].—The compound $\mathrm{Bu^t{}_2P(CH_2)_2CO_2Et}$ (0.246 g, 1 mmol) was added to a solution of dichlorobis(trimethylacetonitrile)platinum(II) (0.432 g, 1 mmol) in dichloromethane. The solvent was evaporated, the resulting residue dissolved in toluene, and the solution was heated under reflux for 1 min to give an orange solution. The solvent was removed and the residue was dissolved in warm ethanol, from whence orange microprisms formed on cooling, yield 43%, m.p. 227—234 °C (decomp.). *Di-μ-chloro-bis*-[*chloro(ethyl 4-di-t-butylphosphinobutyrate)platinum*(II)] was prepared similarly, yield 38%, m.p. 146 °C.

Di-μ-chloro-bis[*(3-di-t-butylphosphino-*1*-ethoxycarbonylpropyl-*C^{1}P*)platinum*(II)] (4).—The compound $\mathrm{Bu^t{}_2P(CH_2)_3CO_2Et}$ (0.260 g, 1 mmol) was added to a solution of $[\mathrm{PtCl_2(NCCMe_3)_2}]$ (0.432 g, 1 mmol) in dichloromethane. The solvent was removed, the residue dissolved in toluene, and the solution was heated under reflux until no more HCl was evolved (3.5 h). The dark brown solution was then shaken with charcoal, filtered, and the solvent was removed. The residue was dissolved in ethanol (5 cm^3), and off-white crystals of the required product (mixture of isomers) slowly precipitated over 3—4 d, yield 63%, m.p. 182—192 °C.

*Chloro(3-di-t-butylphosphino-*1*-ethoxycarbonylpropyl-*C^{1}P*)(triphenylphosphine)platinum*(II) (5).—Complex (4) (0.150 g, 0.153 mmol) in dichloromethane (5 cm^3) was treated with triphenylphosphine (0.080 g, 0.305 mmol). Light petroleum (b.p. 60—80 °C, 5 cm^3) was added to the resulting solution. The required product separated as white prisms (0.194 g, 84%).

*Chloro(diphenylphosphinoacetic acid)(diphenylphosphinoacetato-*OP*)-palladium*(II) *and -platinum*(II).—Diphenylphosphinoacetic acid (250 mg, 1.02 mmol) and $[\mathrm{PdCl_2(NCPh_2)}]$ (19 mg, 0.5 mmol) or $[\mathrm{PtCl_2(NCCMe_3)_2}]$ (216 mg, 0.5 mmol) were warmed together in acetone (5 cm^3). The solution was set aside overnight, yielding the *product*: yield 83% (Pd), m.p. 195—196 °C (decomp.); 95% (Pt), m.p. 218—220 °C (decomp.).

*Bis(diphenylphosphinoacetate-*OP*)-palladium*(II) *or -platinum*(II).—The complex $[\overline{\mathrm{MCl(OCOCH_2P}}\mathrm{Ph_2})$-$(\mathrm{Ph_2PCH_2CO_2H})]$ (M = Pd or Pt) (200 mg) was suspended in hot ethanol (5 cm^3) and $\mathrm{Na[O_2CMe]\cdot 2H_2O}$ (100 mg) was added. The solids dissolved and the required product crystallized out on cooling, yields 80%, m.p.s *ca.* 225 °C (decomp.).

Dichlorobis(4-di-t-butylphosphinobutyric acid)-palladium or -platinum(II).—The complex $[\mathrm{MCl_2\{Bu^t{}_2P(CH_2)_3CO_2Et\}_2}]$ (M = Pd or Pt) (200 mg) and potassium hydroxide (100 mg) were suspended in ethanol (5 cm^3). The mixture was warmed for 10 min, cooled, and then acidified with dilute hydrochloric acid to precipitate the product, yields 85%, m.p. 253—256 (Pd), 261—263 °C (Pt).

*Dichlorobis(ethyl di-t-butylphosphinoacetate-*OP*)rhodium*(III) *Tetraphenylborate*.—A solution of rhodium(III) trichloride (0.165 g, 0.632 mmol) in ethanol (25 cm^3) was treated with $\mathrm{Bu^t{}_2PCH_2CO_2Et}$ (0.734 g, 3.16 mmol) and the resulting mixture was shaken for 24 h. Sodium tetraphenylborate (0.82 g, 2.4 mmol) was then added to give the *product* (0.216 g) as orange needles, yield 36%, m.p. 134—140 °C.

Bis(ethyl di-t-butylphosphinoacetate)dihydrido(tetrahydroborato)rhodium(III).—A solution of $\mathrm{RhCl_3}$ (0.325 g, 1.25 mmol) in ethanol (40 cm^3) containing $\mathrm{Bu^t{}_2PCH_2CO_2Et}$ (0.867 g, 3.74 mol) was shaken for 3 h then cooled to 0 °C. Sodium tetrahydroborate (0.200 g) was added in portions (10 mg) to give a cream suspension. This was evaporated to dryness and the residue was extracted with diethyl ether and water. Dilution of the organic layer with light petroleum (b.p. 60—80 °C) gave the *product* (0.326 g, 45%) as white prisms, m.p. 86—90 °C.

Dichlorobis(ethyl 3-di-t-butylphosphinopropionate)rhodium(II).—Rhodium trichloride (0.140 g, 0.5 mmol) was dissolved in warm degassed ethanol, the solution was cooled, and $\mathrm{Bu^t{}_2P(CH_2)_2CO_2Et}$ (0.6 g, 2.5 mmol) was then added. After the initial fibrous orange precipitate had redissolved, the solution was cooled to 0 °C and gradually yielded blue prisms of the product, yield 72%, m.p. 145—147 °C. *Dichlorobis(ethyl 4-di-t-butylphosphinobutyrate)rhodium*(II) was prepared similarly as green microcrystals, yield 85%, m.p. 90—96 °C.

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