

The preparation and coordination chemistry of phosphorus(III) derivatives of dialkyl ureas and thioureas

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The preparation of $\text{Ph}_2\text{PNEtC(O)NEtPPh}_2$ and $\text{Ph}_2\text{PNMeC(S)NMePPh}_2$ is reported. The coordination chemistry of $\text{Ph}_2\text{PNEtC(O)NEtPPh}_2$, $\text{Ph}_2\text{PNMeC(O)NMePPh}_2$ and $\text{Ph}_2\text{PNMeC(S)NMePPh}_2$ with Pt(II) and Pd(II) has been studied. The urea derivatives react with $\text{MCl}_2(\text{cod})$ ($\text{M} = \text{Pd}, \text{Pt}$) to give simple MCl_2L complexes. Demonstrative examples of simple chelate $\text{Mo(CO)}_4\text{L}$ and bimetallic ClAu-L-AuCl complexes have also been prepared. However with Pd(OAc)_2 bimetallic compounds $[\text{PdOPh}_2\{\text{N(Me)C(O)N(Me)PPh}_2\}]_2$ containing hydrolysed ligands (P–N bond cleaved) are formed. Furthermore the thiourea compound reacts with $\text{PtCl}_2(\text{cod})$ to give $[\text{Pt}\{\text{Ph}_2\text{PN(Me)-C(N(Me)HS)}\}\text{Cl}_2]$, a true heterocycle containing a PtSCNP ring. The new compounds have been characterised spectroscopically and the X-ray structures of six complexes are reported.

After initial investigations in the 1960's,^{1,2} research into diphosphines based on urea and thiourea backbones became dormant until interest was recently rekindled.^{3–8} The mild reaction conditions required in the synthesis of these ligands coupled with the inexpensive nature of the starting materials ensures that the products remain economically viable for applications in catalysis, while the substituent groups on both the phosphorus and the nitrogen atoms can be easily varied, offering excellent control of the steric and electronic properties of the ligands. The presence of the C=O and C=S functionalities also offers sites which can be chemically modified to alter the properties of the compounds. Here we report on the coordination properties of the known compounds, as well as the synthesis and coordination chemistry of new diphosphine derivatives of dialkylureas and thioureas. Some aspects of this work have appeared in a preliminary communication.⁹

Experimental

General experimental conditions and instrumentation were as previously reported.^{10,11} $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene),¹² $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pt}$ or Pd ; cod = cycloocta-1,5-diene),^{13,14} $[\text{PtMeX}(\text{cod})]$ ($\text{X} = \text{Cl}$ or Me),¹⁵ $[\text{Mo(CO)}_4(\text{pip})_2]$ (pip = piperidine),¹⁶ and $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$,¹⁷ were prepared using literature procedures. Chlorodiphenylphosphine and triethylamine were distilled prior to use. *N,N'*-Dimethylurea, *N,N'*-diethylurea, *N,N'*-diethylthiourea, P_2O_5 , AgClO_4 and reagent grade KBr were used without further purification. Pd(OAc)_2 was kindly donated by BP Chemicals Ltd.

Syntheses

$[\text{Ph}_2\text{PN(Me)}]_2\text{CO}$ 1. A solution of *N,N'*-dimethylurea (2.00 g, 22.7 mmol) and triethylamine (4.59 g, 6.5 cm³, 45.4 mmol) in dichloromethane (20.0 cm³) was added dropwise over a period of 3 h to a stirred solution of chlorodiphenylphosphine (9.94 g, 8.2 cm³, 35 mmol) in dichloromethane (10.0 cm³). Stirring was continued for 24 h. The solvent was removed *in vacuo* and diethyl ether (20.0 cm³) added. The white solid was collected by suction filtration, washed with water to remove triethylamine hydrochloride and dried over P_4O_{10} *in vacuo*. Yield: 5.76 g, 56%.

$[\text{Ph}_2\text{PN(Et)}]_2\text{CO}$ 2. A solution of *N,N'*-diethylurea (2.00 g, 17.2 mmol) and triethylamine (3.63 g, 5.0 cm³, 35.0 mmol) in dichloromethane (20.0 cm³) was added dropwise over a period of 4 h to a stirred solution of chlorodiphenylphosphine (7.57 g, 6.2 cm³, 35.0 mmol) in dichloromethane (10.0 cm³). Stirring was continued for 48 h. The solvent was removed *in vacuo* and diethyl ether (20.0 cm³) added. The white solid was collected by suction filtration, washed with water to remove triethylamine hydrochloride and dried over P_4O_{10} *in vacuo*. Yield: 3.35 g, 40%.

***cis*- $[\text{PtCl}_2\{\text{Ph}_2\text{PN(Me)CON(Me)PPh}_2\}]$ 3.** To a solution of $[\text{PtCl}_2(\text{cod})]$ (0.033 g, 0.08 mmol) in dichloromethane (5.0 cm³) was added solid $[\text{Ph}_2\text{PN(Me)}]_2\text{CO}$ (0.040 g, 0.08 mmol) and the colourless solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.050 g, 79%.

***cis*- $[\text{PtCl}_2\{\text{Ph}_2\text{PN(Et)CON(Et)PPh}_2\}]$ 4.** To a solution of $[\text{PtCl}_2(\text{cod})]$ (0.038 g, 0.10 mmol) in dichloromethane (5.0 cm³) was added solid $[\text{Ph}_2\text{PN(Et)}]_2\text{CO}$ (0.050 g, 0.10 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.045 g, 58%.

***cis*- $[\text{PtMe}_2\{\text{Ph}_2\text{PN(Me)CON(Me)PPh}_2\}]$ 5.** To a solution of $[\text{PtMe}_2(\text{cod})]$ (0.044 g, 0.13 mmol) in dichloromethane (10.0 cm³) was added solid $[\text{Ph}_2\text{PN(Me)}]_2\text{CO}$ (0.060 g, 0.13 mmol) and the colourless solution stirred for *ca.* 3 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and light petroleum (bp 60–80 °C) (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.058 g, 65%.

***cis*- $[\text{PtMe}_2\{\text{Ph}_2\text{PN(Et)CON(Et)PPh}_2\}]$ 6.** To a solution of $[\text{PtMe}_2(\text{cod})]$ (0.034 g, 0.10 mmol) in dichloromethane (5.0 cm³) was added solid $[\text{Ph}_2\text{PN(Et)}]_2\text{CO}$ (0.050 g, 0.10 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and light petroleum (bp 60–80 °C) (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.046 g, 63%.

cis-[PtMe(Cl){Ph₂PN(Me)CON(Me)PPh₂}] 7. To a solution of [PtMe(Cl)(cod)] (0.054 g, 0.15 mmol) in dichloromethane (10.0 cm³) was added solid [Ph₂PN(Me)]₂CO (0.070 g, 0.15 mmol) and the colourless solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.075 g, 67%.

cis-[PtMe(Cl){Ph₂PN(Et)CON(Et)PPh₂}] 8. To a solution of [PtMe(Cl)(cod)] (0.036 g, 0.10 mmol) in dichloromethane (5.0 cm³) was added solid [Ph₂PN(Et)]₂CO (0.050 g, 0.10 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The white product was collected by suction filtration. Yield: 0.049 g, 63%.

cis-[PdCl₂{Ph₂PN(Me)CON(Me)PPh₂}] 9. To a yellow solution of PdCl₂(cod) (0.033 g, 0.08 mmol) in dichloromethane (10.0 cm³) was added solid [Ph₂PN(Me)]₂CO (0.040 g, 0.08 mmol) and the yellow solution stirred for *ca.* 3 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The yellow product was collected by suction filtration. Yield: 0.040 g, 73%.

cis-[PdCl₂{Ph₂PN(Et)CON(Et)PPh₂}] 10. To a yellow solution of [PdCl₂(cod)] (0.029 g, 0.10 mmol) in dichloromethane (5.0 cm³) was added solid [Ph₂PN(Et)]₂CO (0.050 g, 0.10 mmol) and the yellow solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The yellow product was collected by suction filtration. Yield: 0.050 g, 73%.

[Pd{OPPh₂}{N(Me)C(O)N(Me)PPh₂}]₂ 11. To a yellow solution of [Pd(OAc)₂] (0.150 g, 0.70 mmol) in dichloromethane (10.0 cm³) was added solid [Ph₂PN(Me)]₂CO (0.320 g, 0.70 mmol) and the dark yellow solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10.0 cm³) added. The dark yellow product was collected by suction filtration. Yield: 0.251 g, 31%. IR (KBr disc, cm⁻¹): 3052w, 2915w, 1630vs, 1610vs, 1480w, 1434s, 1325s, 1208w, 1105vs, 1010vs, 995vs, 948w, 815w, 744s, 692vs, 595w, 552vs, 535s, 508vs, 492s and 345w.

[Pd{OPPh₂}{N(Et)C(O)N(Et)PPh₂}]₂ 12. To a yellow solution of [Pd(OAc)₂] (0.045 g, 0.2 mmol) in dichloromethane (5.0 cm³) was added solid [Ph₂PN(Me)]₂CO (0.100 g, 0.02 mmol) and the dark yellow solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1 cm³ and diethyl ether (10 cm³) added. The dark yellow product was collected by suction filtration. Yield: 0.127 g, 51%. IR (KBr disc, cm⁻¹): 3053w, 2927w, 1672w, 1620vs, 1481w, 1435s, 1369w, 1319s, 1281s, 1219w, 1181s, 1103s, 1034s, 1022s, 996s, 746s, 695vs, 593w, 553vs, 529s, 505s, 472w and 328w.

cis-[Mo(CO)₄{Ph₂PN(Me)CON(Me)PPh₂}] 13. To a partially dissolved solution of [Mo(CO)₄(pip)₂] (0.580 g, 1.50 mmol) in dichloromethane (20.0 cm³) was added solid [Ph₂PN(Me)]₂CO (0.700 g, 1.50 mmol). The solution was heated to reflux for *ca.* 15 min and allowed to cool to room temperature. The solution was concentrated under reduced pressure to *ca.* 2.0 cm³ and methanol (15.0 cm³) added. The yellow product was collected by suction filtration. Yield: 0.725 g, 71%.

cis-[Rh(cod){Ph₂PN(Et)CON(Et)PPh₂}]⁺[ClO₄]⁻ 14. To a stirred solution of [RhCl(cod)]₂ (0.050 g, 0.10 mmol) in acetone (20.0 cm³) was added AgClO₄ and the solution stirred for 15 min. The colourless precipitate was removed by filtration and washed with acetone (10.0 cm³). To the combined filtrates and washings was added solid [Ph₂PN(Et)]₂CO (0.098 g, 0.20 mmol) and the solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether

(5.0 cm³) added. The brown product was collected by suction filtration. Yield: 0.092 g, 58%.

[Ph₂P(AuCl)N(Et)CON(Et)P(AuCl)Ph₂]] 15. To a solution of [AuCl(tht)] (0.032 g, 0.10 mmol) in dichloromethane (10.0 cm³) was added solid [Ph₂PN(Et)]₂CO (0.050 g, 0.10 mmol) and the colourless solution stirred for *ca.* 15 min. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (5.0 cm³) added. The colourless product was collected by suction filtration. Yield: 0.069 g, 72%.

[Ph₂PN(Et)]₂CS 16. A solution of chlorodiphenylphosphine (5.0 g, 4.1 cm³, 22.7 mmol) in diethyl ether (20.0 cm³) was added dropwise over a period of 45 min to a stirred solution of *N,N'*-diethylthiourea (3.00 g, 22.7 mmol) and triethylamine (4.60 g, 6.3 cm³, 35.0 mmol) in diethyl ether (100.0 cm³) and thf (20.0 cm³) at -5 °C. The reaction mixture was then allowed to warm to room temperature and stirring continued for 72 h during which time triethylammonium hydrochloride separated from the colourless solution. A second solution of chlorodiphenylphosphine (5.0 g, 4.1 cm³, 22.7 mmol) in diethyl ether (20.0 cm³) was added to the reaction mixture and stirring continued for a further 48 h. Triethylammonium hydrochloride was removed by suction filtration and reduction of the solvent volume *in vacuo* resulted in precipitation of the product as a white solid. Yield: 2.94 g, 26%.

[PtCl₂{Ph₂PN(Me)CSN(Me)H}] 17. To a solution of [PtCl₂(cod)] (0.040 g, 0.10 mmol) in dichloromethane (5.0 cm³) was added solid [Ph₂PN(Me)]₂CS (0.050 g, 0.10 mmol) and the pale yellow solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm³ and diethyl ether (10 cm³) added. The pale yellow product was collected by suction filtration. Yield: 0.050 g, 85%. IR (KBr disc, cm⁻¹): 3222w, 3052w, 1577vs, 1482m, 1436vs, 1376s, 1325vs, 1218w, 1185w, 1142w, 1106vs, 1059m, 997m, 829s, 747s, 718m, 691s, 578s, 541m, 521m, 490s, 318w, 290m, 3235m, 221vs and 210vs. FAB mass spectrum: *m/z* 519, [M - Cl]⁺.

Crystallography

Crystallography (Table 1) was performed using a Bruker SMART diffractometer; full hemisphere of data with 0.3° 'slices', room temperature, Mo-K α radiation and empirical absorption corrections. All non-H atoms were refined anisotropically, H atoms were idealised. All calculations employed the SHELXTL program system.¹¹ The poor quality of crystals for **12** precluded any improvement in the quality of this structure—several different crystals were examined with no improvement. Details for **9**, **11** and **17** have already been reported.⁹

CCDC reference numbers 168899–168904.

See <http://www.rsc.org/suppdata/dt/b1/b104122n/> for crystallographic data in CIF or other electronic format.

Results and discussion

Both ourselves¹⁸ and Schmutzler³⁻⁸ have reported the synthesis of diphosphine derivatives of ureas from silylated starting materials. We have now discovered that the synthesis of [Ph₂PN(Me)]₂CO **1** is also possible from the reaction of *N,N'*-dimethylurea with two equivalents of Ph₂PCl, in the presence of NEt₃, in dichloromethane [eqn. (1)].

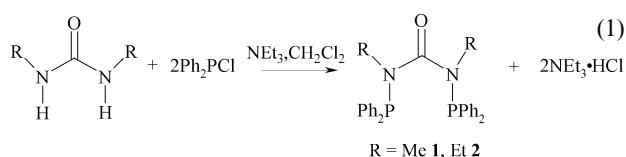


Table 1 Details of X-ray data collection and refinements

Compound	3	4	11	12	13	15
Empirical formula	C ₂₇ H ₂₆ Cl ₂ N ₂ -OP ₂ Pt	C ₂₉ H ₃₀ Cl ₂ N ₂ -OP ₂ Pt	C ₃₇ H ₄₂ Cl ₄ N ₂ -OP ₂ Pd ₂	C ₅₉ H ₆₂ N ₄ O ₄ P ₄ -Pd ₂ Cl ₂	C ₃₁ H ₂₆ N ₂ O ₅ -P ₂ Mo	C ₃₀ H ₃₁ Cl ₅ N ₂ -OP ₂ Au ₂
Formula weight	722.4	750.5	947.3	1298.7	664.4	1068.7
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ <i>cn</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.0447(5)	9.8640(4)	14.2866(3)	10.4350(2)	12.0547(1)	14.5596(5)
<i>b</i> /Å	14.4768(7)	10.8209(4)	27.6453(5)	18.7436(3)	17.0186(2)	15.4267(5)
<i>c</i> /Å	18.5427(9)	15.1644(6)	9.7662(2)	15.6919(1)	14.662(1)	16.1541(5)
<i>α</i> /°	90	78.430(1)	90	90	90	90
<i>β</i> /°	90	80.056(1)	92.632(1)	94.362(1)	94.485(1)	98.36(1)
<i>γ</i> /°	90	66.664(1)	90	90	90	90
<i>V</i> /Å ³	2696	1448	3853	3060	2999	3590
<i>Z</i>	4	2	4	2	4	4
Density (calc.)/Mg m ⁻³	1.78	1.72	1.63	1.41	1.47	1.98
Observed ind. refl.	2605	5727	4874	1785	3487	5380
[<i>I</i> > 2.0σ(<i>I</i>)]						
Final <i>R</i> , <i>R</i> _w	0.0209, 0.0389	0.0257, 0.0590	0.0470, 0.1041	0.1033, 0.2379	0.0251, 0.0609	0.0354, 0.0752

Table 2 Elemental analyses and selected spectroscopic data (calculated values in parentheses)

Formula	δ_P (ppm)/ ¹ <i>J</i> (Hz)	<i>m/z</i>	$\nu(\text{CO})$ / cm ⁻¹	$\nu(\text{CN})$ / cm ⁻¹	$\nu(\text{PN})$ / cm ⁻¹	C (%)	H (%)	N (%)
1 [Ph ₂ PN(Me)] ₂ CO	54.6	456	1646	1432	961	70.6 (71.0)	5.3 (5.7)	5.8 (6.1)
2 [Ph ₂ PN(Et)] ₂ CO	56.1	484	1649	1432	992	70.8 (71.2)	6.2 (6.2)	5.3 (5.8)
3 [PtCl ₂ {(Ph ₂ PN(Me)) ₂ CO}]	53.4/3792	722	1672	1435	973	44.8 (44.9)	3.4 (3.6)	3.6 (3.8)
4 [PtCl ₂ {(Ph ₂ PN(Et)) ₂ CO}]	56.7/3910	715 [–Cl]	1669	1436	997	46.2 (46.4)	4.2 (4.0)	3.9 (3.7)
5 [PtMe ₂ {(Ph ₂ PN(Me)) ₂ CO}]	74.9/1944	681	1626	1434	983	49.3 (50.1)	4.9 (5.1)	4.0 (4.2)
6 [PtMe ₂ {(Ph ₂ PN(Et)) ₂ CO}]	77.7/1997	710	1652	1436	994	52.7 (52.4)	5.8 (5.1)	4.0 (3.9)
7 [PtCl(Me){(Ph ₂ PN(Me)) ₂ CO}]	74.1/1819; 61.4/4509 ^a	701	1637	1433	984	47.5 (47.9)	4.0 (4.2)	3.7 (3.9)
8 [PtCl(Me){(Ph ₂ PN(Et)) ₂ CO}]	77.1/1891; 64.2/4596 ^a	730	1658	1436	996	48.8 (49.3)	4.0 (4.5)	3.1 (3.8)
9 [PdCl ₂ {(Ph ₂ PN(Me)) ₂ CO}]	76.2	598 [–Cl]	1648	1435	991	50.9 (51.2)	3.8 (4.1)	3.9 (4.4)
10 [PdCl ₂ {(Ph ₂ PN(Et)) ₂ CO}]	80.1	626 [–Cl]	1670	1436	996	52.8 (52.6)	4.4 (4.5)	3.8 (4.2)
11 [Pd{OPPh ₂ }{N(Me)C(O)N(Me)PPh ₂ }] ₂	71.2; 84.4	1158	1630	1434/1325	995	56.1 (55.5)	4.3 (4.5)	4.3 (4.8)
12 [Pd{OPPh ₂ }{N(Et)C(O)N(Et)PPh ₂ }] ₂	69.5; 84.4	1214	1620	1435/1319	996	56.8 (57.4)	4.6 (5.0)	4.0 (4.6)
13 [Mo(CO) ₄ {(Ph ₂ PN(Me)) ₂ CO}]	101.9	664	1643	1433	962	55.4 (56.0)	3.8 (3.9)	4.1 (4.2)
14 [Rh(cod){(Ph ₂ PN(Et)) ₂ CO}][ClO ₄]	90.3/167	695 [–ClO ₄]	1664	1437	996	58.7 (58.9)	5.1 (5.3)	3.4 (3.5)
15 [(AuCl) ₂ {(Ph ₂ PN(Et)) ₂ CO}]	75.7	949	1655	1436	997	36.9 (36.6)	3.6 (3.2)	3.2 (2.9)
16 [Ph ₂ PN(Et)] ₂ CS	67.8	468 [–S]	1174 ^b	1435	997	69.3 (69.6)	6.0 (6.0)	5.3 (5.6)
17 [Pt{Ph ₂ PN(Me)C(N(Me)HS)}Cl ₂]	78.3/3967	519 [–Cl]	1059 ^b	1436	997	32.1 (32.4)	2.9 (3.1)	4.8 (5.1)

^a ²*J*(PP) 31 Hz. ^b $\nu(\text{CS})$.

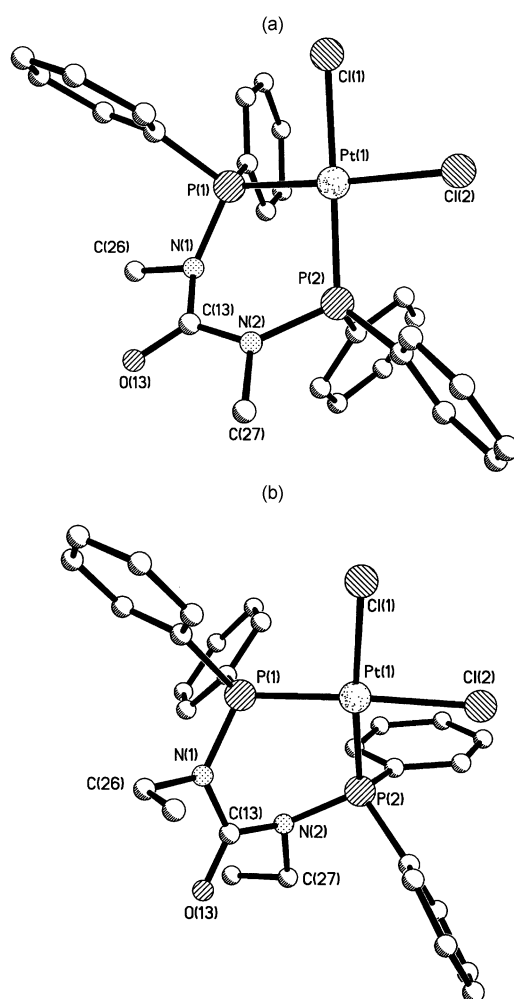
Slow addition of a dichloromethane solution of {HN(Me)}₂-CO and NEt₃ to a dichloromethane solution of Ph₂PCl at room temperature results in a viscous, pale yellow solution. ³¹P-¹H NMR studies conducted on the methylurea reaction immediately after completion of the addition of the urea show that the reaction mixture contains three phosphorus-containing species, the starting material Ph₂PCl, at δ_P 82.9, the desired product **1**, at δ_P 54.6, and presumably the mono-substituted product {Ph₂P-N(Me)C(O)N(Me)H} at δ_P 46.4. We can be confident in this assignment as the value of its chemical shift, δ_P 46.4, and its position relative to the bis-substituted product are analogous to the values for mono-substituted products of similar, related thiourea systems.¹⁹ Stirring the reaction mixture overnight results in the loss of the species at δ_P 82.9 and δ_P 46.4 and leaves **1** as the only phosphorus-containing species. Removal of the solvent *in vacuo*, leaves an off white solid residue which is washed with water to remove NEt₃·HCl. Collection of the solid by suction filtration and drying over P₄O₁₀ *in vacuo* results in the product, **1**, as a white solid in 56% yield. Air- and moisture-tolerant, **1** is readily soluble in both dichloromethane and thf. Elemental analysis is in good agreement with the calculated values (Table 2) and FAB⁺ mass spectrometry shows the expected parent-ion peak (*m/z* 456 [M]⁺). The IR spectrum of **1** contains strong bands which can be assigned to $\nu(\text{CO})$, $\nu(\text{CN})$ and $\nu(\text{PN})$ (Table 2).

As mentioned above, Schmutzler and co-workers have reported the synthesis of phosphine derivatives of *N,N'*-dimethylurea.^{3–8} However, reports of metal complexes containing these ligands are rare, especially where the ligands act as *P,P'* chelates. Therefore, using **1** and **2**, we have investigated their complexation chemistry more fully *via* reactions with various metal compounds.

The reactions of **1** and **2** with equimolar quantities of [PtCl₂(cod)] in dichloromethane proceed smoothly to yield the *P,P'*-chelates *cis*-[PtCl₂{(Ph₂PN(Me))₂CO}], **3**, and *cis*-[PtCl₂{(Ph₂PN(Et))₂CO}], **4** as six-membered metallacycles, spectroscopic properties are summarised in Table 2. The magnitude of the ¹*J*(¹⁹⁵Pt–³¹P) couplings (3792 for **3** and 3910 Hz for **4**) are in agreement with reported values for similar diphosphine urea chelates containing a phosphorus *trans* to chloride in Pt(II) systems.²⁰ The IR spectra of **3** and **4** show bands which can be assigned to $\nu(\text{CO})$, $\nu(\text{CN})$ and $\nu(\text{PN})$ (Table 2); $\nu(\text{CO})$ is shifted slightly to higher frequency upon complexation. Single crystal X-ray studies confirm the *cis* chelate geometry of the ligands and that the molecules are square planar at the platinum (Fig. 1, Table 3). The molecules have approximate *C*₂ symmetry and the bite angles are close to 90° [90.7(2) for **3** and 88.8(3)° for **4**] indicating that this size ring is very well suited to square planar coordination. In **3** the six-membered PtP₂N₂C ring is hinged about P(2)–N(1) by 45° while in **4** the same ring is

Table 3 Selected bond lengths (Å) and angles (°) for compounds **3**, **4**, **9** and **10**

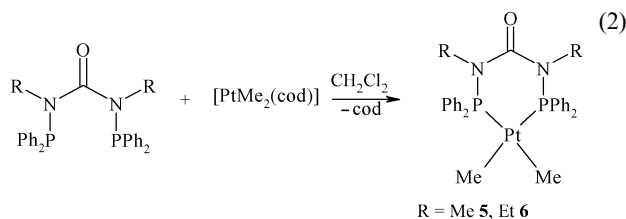
	3	4	9	10
P(1)–M(1)	2.207(4)	2.2141(8)	2.2003(8)	2.2165(13)
P(2)–M(1)	2.2054(13)	2.2157(8)	2.2072(8)	2.2135(13)
M(1)–Cl(1)	2.3567(13)	2.3414(9)	2.3476(8)	2.3545(13)
M(1)–Cl(2)	2.362(4)	2.3595(9)	2.3418(9)	2.3577(13)
N(1)–P(1)	1.716(6)	1.725(3)	1.697(2)	1.707(4)
N(2)–P(2)	1.749(8)	1.714(3)	1.704(2)	1.712(4)
N(1)–C(13)	1.413(10)	1.385(5)	1.380(4)	1.382(6)
N(2)–C(13)	1.360(12)	1.411(5)	1.377(4)	1.397(6)
N(1)–C(26)	1.499(8)	1.488(5)	1.494(4)	1.506(6)
N(2)–C(27)	1.485(8)	1.500(5)	1.486(4)	1.504(6)
C(13)–O(13)	1.222(11)	1.217(5)	1.224(3)	1.215(6)
P(1)–M(1)–P(2)	90.7(2)	88.8(3)	94.76(3)	91.47(5)
N(1)–P(1)–M(1)	114.9(2)	111.0(11)	118.19(9)	115.93(14)
N(2)–P(2)–M(1)	112.0(3)	114.8(11)	118.41(9)	116.05(14)
Cl(1)–M(1)–Cl(2)	89.4(14)	87.9(4)	91.47(3)	90.28(5)
Cl(1)–M(1)–P(1)	86.9(14)	95.5(3)	86.84(3)	89.26(5)
Cl(2)–M(1)–P(2)	92.7(2)	87.7(3)	86.98(3)	89.22(5)
P(1)–N(1)–C(13)	125.1(6)	122.5(2)	132.6(2)	126.2(3)
P(2)–N(2)–C(13)	123.5(6)	120.6(2)	131.5(2)	117.2(3)
N(1)–C(13)–N(2)	119.8(8)	117.8(3)	122.9(3)	120.2(4)
N(1)–C(13)–O(13)	118.8(9)	121.0(4)	118.6(3)	120.7(4)
N(2)–C(13)–O(13)	121.1(9)	121.1(4)	118.5(3)	119.1(4)
C(13)–N(2)–C(27)	116.1(7)	112.5(3)	112.8(2)	113.2(4)
C(13)–N(1)–C(26)	111.7(6)	115.1(3)	112.4(4)	112.9(4)

**Fig. 1** (a) Solid state structure of *cis*-[PtCl₂{Ph₂PN(Me)₂CO}] **3**. (b) Solid state structure of *cis*-[PtCl₂{Ph₂PN(Et)₂CO}] **4**.

hinged about P(1)–N(2) by 51°. In both molecules the exocyclic urea oxygen atom is effectively in the plane of its substituents. The internal angles of the rings in both **3** and **4** are all close to trigonal and it is noticeable in both molecules that the C–N

bond lengths within the PtP₂N₂C ring are significantly shorter than N–Me/N–Et bond lengths, indicating some degree of delocalisation across the N₂C=O groups. In both complexes the P–N bond lengths [1.716(6) and 1.749(8) Å for **3** and 1.725(3) and 1.714(3) Å for **4**] are similar to those observed in related compounds.^{18,20}

Both {Ph₂PN(Me)₂}₂CO and {Ph₂PN(Et)₂}₂CO also react successfully with [PtMe₂(cod)] to produce *P,P'* chelates [eqn. (2)] and with [PtCl(Me)(cod)] to give *cis*-[PtCl(Me)–



{Ph₂PN(Me)₂}₂CO}], **7** and *cis*-[PtCl(Me){Ph₂PN(Et)₂CO}], **8** respectively.

Palladium complexes involving [Ph₂PN(Me)₂]CO and [Ph₂PN(Et)₂]CO acting as bidentate *P,P'* chelates are also successfully formed when the diphosphines **1** and **2** are reacted with [PdCl₂(cod)]. In the solid state structures of *cis*-[PdCl₂{Ph₂PN(Me)₂CO}] **9** and *cis*-[PdCl₂{Ph₂PN(Et)₂CO}] **10** the molecules have approximate non-crystallographic C₂ symmetry and similar geometry about the metal to **3** and **4**. Perhaps the most surprising difference is an enlargement of the P–N–C angles in **9** and **10** relative to those in **3** and **4**, for which there is no ready explanation. In **9** the PdP₂N₂C ring is effectively planar and co-planar with the coordination sphere. The same ring in **10** is puckered, though not hinged like the examples in **3** and **4**, with C(13) and O(13) in the same plane as the coordination sphere and N(1) and N(2) lying 0.5 Å above and below the plane respectively. As with compounds **3** and **4** the P–N bond lengths in **9** and **10** [1.697(2) and 1.704(2) Å for **9** and 1.707(4) and 1.712(4) Å for **10**] are within the expected range²⁰ and, once again, the C–N bond lengths within the PtP₂N₂C rings of both molecules are significantly shorter than the N–Me/N–Et bond lengths, indicating some degree of delocalisation across the N₂C=O groups. The Pd–Cl and Pd–P bond lengths in **9** and **10** are normal.

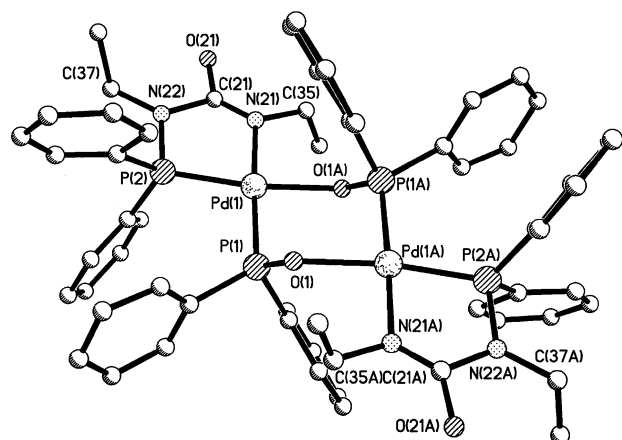
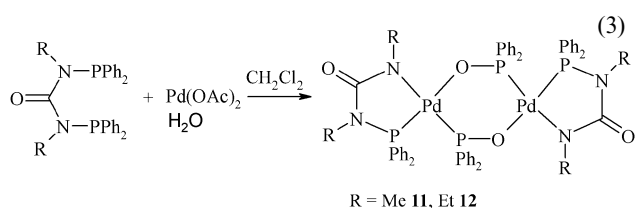


Fig. 2 Solid state structure of $[\text{Pd}\{\text{OPPh}_2\}\{\text{N}(\text{Et})\text{C}(\text{O})\text{N}(\text{Et})\text{PPh}_2\}]_2 \cdot \text{CH}_2\text{Cl}_2$ **12**; **11** has a very similar structure and is not reproduced.

Table 4 Selected bond lengths (Å) and angles (°) for **11**

Pd(1)–N(2)	2.083(4)	Pd(2)–N(32)	2.059(4)
Pd(1)–P(1)	2.2043(14)	Pd(2)–P(31)	2.1985(14)
Pd(1)–O(32)	2.092(3)	Pd(2)–O(2)	2.075(3)
Pd(1)–P(2)	2.2764(14)	Pd(2)–P(31)	2.2600(14)
P(1)–N(1)	1.674(5)	P(31)–N(31)	1.676(5)
N(1)–C(13)	1.424(7)	N(31)–C(43)	1.414(7)
C(13)–N(2)	1.323(7)	C(43)–N(32)	1.328(7)
C(13)–O(13)	1.235(6)	C(43)–O(43)	1.240(6)
P(2)–O(2)	1.536(4)	P(32)–O(32)	1.539(3)
P(1)–Pd(1)–N(2)	81.81(13)	P(31)–Pd(2)–N(32)	81.90(13)
Pd(1)–P(1)–N(1)	102.6(2)	Pd(2)–P(31)–N(31)	102.3(2)
P(1)–N(1)–C(13)	119.4(3)	C(43)–N(31)–P(31)	119.2(3)
N(1)–C(13)–N(2)	114.6(5)	N(31)–C(43)–N(32)	114.2(5)
C(13)–N(2)–Pd(1)	121.6(4)	C(43)–N(32)–Pd(2)	121.9(4)
Pd(1)–P(2)–O(2)	113.9(2)	Pd(2)–P(32)–O(32)	112.8(2)
Pd(1)–O(32)–P(32)	128.4(7)	Pd(2)–O(2)–P(2)	134.8(2)

Compounds **9** and **10** demonstrate that the ligands $[\text{Ph}_2\text{P}(\text{N}(\text{Me})_2\text{CO})]$ **1** and $[\text{Ph}_2\text{PN}(\text{Et})_2\text{CO}]$ **2** can act as simple metal chelates and form six-membered ring systems when reacted with $[\text{PdCl}_2(\text{cod})]$. However, reaction of the two ligands with palladium acetate fails to result in the expected chelate systems. Instead P–N bond cleavage takes place and the reaction involves the formation of a $[\text{Ph}_2\text{PO}]^-$ ligand which is incorporated into a $\text{Pd}_2\text{P}_2\text{O}_2$ heterocycle [eqn. (3)]. It seems likely that



the P–N cleavage is acid catalysed by the acetate, with water from the palladium acetate providing the source of oxygen for the hydrolysis.

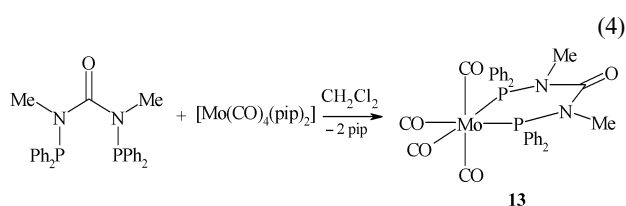
The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **11** shows two broad singlet peaks at δ_{p} 84.4 and δ_{p} 71.2. We assign the phosphorus in the $[\text{Ph}_2\text{PO}]^-$ ligand to the species further downfield at δ_{p} 84.4 due to its proximity to the electronegative oxygen atom and consequently the phosphorus in the PNCNPd ring is assigned to the peak at δ_{p} 71.2. FAB⁺ mass spectrometry shows the parent-ion peak (m/z 1158 $[\text{M}]^+$) and a peak corresponding to $[\text{Pd}\{\text{OPPh}_2\}\{\text{N}(\text{Me})\text{C}(\text{O})\text{N}(\text{Me})\text{PPh}_2\}]^+$ (m/z 579) and the IR spectrum shows peaks which can be assigned to $\nu(\text{CO})$ (1630 cm^{-1}), $\nu(\text{CN})$ (1434 cm^{-1}) and $\nu(\text{PN})$ (995 cm^{-1}). Elemental analysis is in good agreement with calculated values. The solid state structure of $[\text{Pd}\{\text{OPPh}_2\}\{\text{N}(\text{Me})\text{C}(\text{O})\text{N}(\text{Me})\text{PPh}_2\}]_2$ (Fig. 2, Table 4) reveals the square planar palladium centres as

Table 5 Selected bond lengths (Å) and angles (°) for **12**· CH_2Cl_2

Pd(1)–N(21)	1.990(11)	P(2)–N(22)	1.639(12)
Pd(1)–P(1)	2.221(4)	N(22)–C(21)	1.43(2)
Pd(1)–O(1A)	2.051(9)	C(21)–N(21)	1.21(2)
Pd(1)–P(2)	2.160(5)	C(21)–O(21)	1.28(2)
P(2)–Pd(1)–N(21)	80.6(4)	C(21)–N(21)–Pd(1)	124.3(12)
Pd(1)–P(2)–N(22)	103.2(5)	Pd(1)–P(1)–O(1A)	112.7(4)
P(2)–N(22)–C(21)	114.0(12)	N(21)–Pd(1)–O(1A)	92.9(5)
N(22)–C(21)–N(21)	115.7(130)	P(1)–Pd(1)–O(1A)	84.6(4)

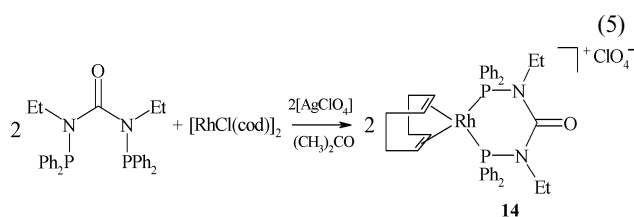
spiro in the tricyclic system. The PdPN_2C rings are close to planar [maximum deviations for the two rings are 0.01 Å for N(2) and –0.05 Å for N(31)] with the C=O and the NMe groups being effectively co-planar with the PdPN_2C rings. The internal nitrogen angles in the PdPN_2C ring are close to trigonal, whilst the angle at the phosphorus is slightly reduced from a perfect tetrahedral angle. The central $\text{Pd}_2\text{P}_2\text{O}_2$ ring adopts a chair geometry with the central $\text{Pd}_2\text{P}_2\text{O}_2$ core having two PdOP planes inclined by *ca.* 138°. Within this ring the P–O bond lengths [P(2)–O(2) 1.536(4) and P(32)–O(32) 1.539(3) Å] are appropriate for a coordinated $[\text{Ph}_2\text{PO}]^-$ anion and similar to those reported for a $\text{Pd}_2\text{P}_2\text{O}_2$ ring²¹ but slightly shorter than those reported for $[(\text{Ph}_3\text{P})\text{Pt}(\text{Ph}_2\text{PO})_2\text{Pt}(\text{PPh}_3)]$.²²

Using the same method employed in the preparation of **11**, $[\text{Pd}\{\text{OPPh}_2\}\{\text{N}(\text{Et})\text{C}(\text{O})\text{N}(\text{Et})\text{PPh}_2\}]_2$, **12** was isolated as a yellow solid in 51% yield (Table 5 for bond lengths and angles). The reaction of $[\text{Ph}_2\text{PN}(\text{Me})_2\text{CO}]$, **1** with $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ in dichloromethane results in the displacement of the piperidine molecules and the formation of the *P,P'* chelate complex *cis*- $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PN}(\text{Me})\text{C}(\text{O})\text{N}(\text{Me})\text{PPh}_2\}]$, **13** [eqn. (4)].



The solid state structure of **13** (Table 6, Fig. 3) reveals octahedral geometry at the molybdenum with some contraction of the P(1)–Mo(1)–P(2) angle [80.7(2)°]. The Mo–C distances differ as a consequence of the *trans* ligand, with Mo–C(31) and Mo–C(34) (*trans* to P) being shorter (*ca.* 2.00 Å) than Mo–C(32) and Mo–C(33) (*trans* to carbonyl) (*ca.* 2.03 Å). Unlike **9** the $\text{MoP}_2\text{N}_2\text{C}$ ring is non-planar, being hinged by 55° along the N(2)–P(1) vector. Within the $\text{MoP}_2\text{N}_2\text{C}$ ring the P–N and C–N bond lengths are close to those reported for similar systems.²³

The reaction of two equivalents $[\text{Ph}_2\text{PN}(\text{Et})_2\text{CO}]$, **2** with $[\text{RhCl}(\text{cod})]_2$ in acetone proceeds according to eqn. (5) to yield



the *P,P'* chelate product *cis*- $[\text{Rh}(\text{cod})\{\text{Ph}_2\text{PN}(\text{Et})\text{CON}(\text{Et})\text{PPh}_2\}][\text{ClO}_4]$, **14**.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **14** contains a single phosphorus-containing species at δ_{p} 90.3 with a $^1J(^{103}\text{Rh}-^{31}\text{P})$ coupling of 167 Hz and the FAB⁺ mass spectrum shows a peak corresponding to $[\text{Rh}(\text{cod})\{\text{Ph}_2\text{PN}(\text{Et})\text{CON}(\text{Et})\text{PPh}_2\}]^+$ (m/z 695).

Compounds **3–10**, **13** and **14** demonstrate the ability of the ligands $[\text{Ph}_2\text{PN}(\text{Me})_2\text{CO}]$ and $[\text{Ph}_2\text{PN}(\text{Et})_2\text{CO}]$ to act as

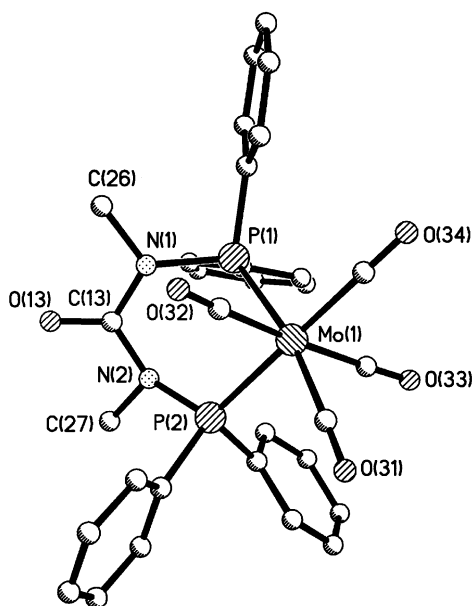
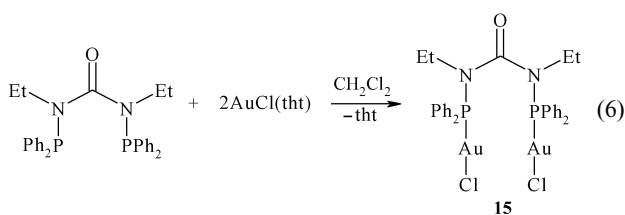


Fig. 3 Solid state structure of *cis*-[Mo(CO)₄{Ph₂PN(Me)C(O)N(Me)PPh₂}] **13**.

Table 6 Selected bond lengths (Å) and bond angles (°) for *cis*-[Mo(CO)₄{Ph₂PN(Me)C(O)N(Me)PPh₂}] **13**

Mo(1)–P(1)	2.4849(7)	P(1)–Mo(1)–P(2)	80.72(2)
Mo(1)–P(2)	2.4808(6)	Mo(1)–P(1)–N(1)	107.69(7)
P(1)–N(1)	1.743(2)	Mo(1)–P(2)–N(2)	116.23(7)
P(2)–N(2)	1.731(2)	P(1)–N(1)–C(13)	123.0(2)
N(1)–C(13)	1.379(3)	P(2)–N(2)–C(13)	124.4(2)
N(2)–C(13)	1.411(3)	N(2)–C(13)–N(1)	118.6(2)
Mo(1)–C(31)	2.003(3)	C(31)–Mo(1)–P(1)	170.25(8)
Mo(1)–C(32)	2.024(3)	C(31)–Mo(1)–P(2)	90.70(8)
Mo(1)–C(33)	2.037(3)	C(34)–Mo(1)–P(1)	97.54(9)
Mo(1)–C(34)	2.001(3)	C(34)–Mo(1)–P(2)	176.29(8)

bidentate *P,P'* chelates and form six-membered metallacycles. Schmutzler and co-workers have also previously reported that [(Ph)(^tBu)PN(Me)₂CO] can act as a bidentate bridging ligand between two metal centres when reacted with [Fe₂(CO)₉].⁸ We have also demonstrated that [Ph₂PN(Et)₂CO] can act as a bidentate bridging ligand when reacted with [AuCl(tht)] to form the complex [Ph₂P{AuCl}N(Et)C(O)N(Et)P{AuCl}Ph₂], **15** [eqn. (6)].



The FAB⁺ mass spectrum shows a parent-ion peak and a peak corresponding to the loss of a chloride ion (*m/z* 949 [M]⁺ and 913 [M – Cl]⁺) and the IR spectrum shows peaks which can be assigned to ν(CO), ν(CN) and ν(PN). The solid state structure of **15** (Fig. 4, Table 7) confirms that the molecule contains two gold centres. The overall W-shaped molecule has approximately non-crystallographic symmetry with a two-fold axis about the C(13)–O(13) bond, though the backbone is non-planar; N(1) and N(2) lie –0.45 and +0.21 Å from the N(1)–C(13)–O(13)–N(2) mean plane. The P–Au–Cl angles are close to linear, as expected, and there is no evidence of any delocalisation in the P₂N₂C chain. P–N, P–Au and Au–Cl bond lengths are all comparable to those observed in similar compounds.²⁴

Both ourselves¹⁸ and Schmutzler and Gruber^{19,25} have

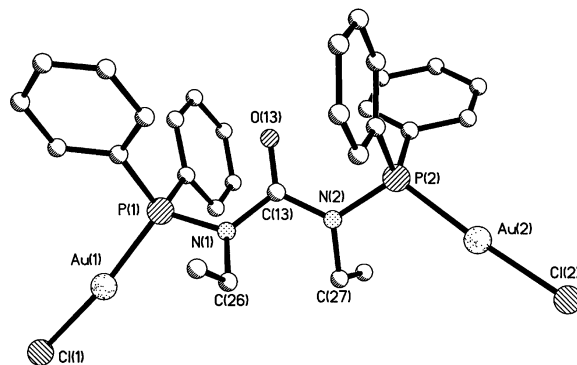


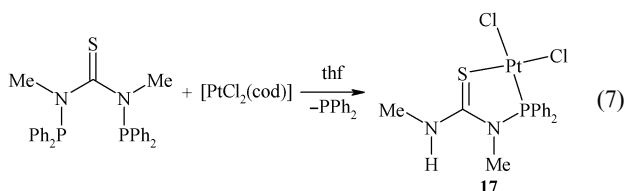
Fig. 4 Solid state structure of [Ph₂P{AuCl}N(Et)C(O)N(Et)P{AuCl}Ph₂] $\cdot$ CHCl₃ **15**.

Table 7 Selected bond lengths (Å) and angles (°) for **15**·CHCl₃

Au(1)–Cl(1)	2.316(2)	P(1)–Au(1)–Cl(1)	171.29(6)
P(1)–Au(1)	2.239(2)	N(1)–P(1)–Au(1)	114.1(2)
P(1)–N(1)	1.709(5)	C(26)–N(1)–P(1)	120.6(4)
N(1)–C(26)	1.475(7)	C(13)–N(1)–P(1)	117.3(4)
N(1)–C(13)	1.415(7)	N(1)–C(13)–O(13)	121.5(5)
C(13)–O(13)	1.213(6)	N(1)–C(13)–N(2)	116.3(5)
C(13)–N(2)	1.389(7)	N(2)–C(13)–O(13)	122.2(5)
N(2)–C(27)	1.492(7)	C(13)–N(2)–P(2)	118.3(4)
N(2)–P(2)	1.706(5)	C(27)–N(2)–P(2)	118.9(4)
P(2)–Au(2)	2.243(2)	N(2)–P(2)–Au(2)	110.1(2)
Au(2)–Cl(2)	2.298(2)	P(2)–Au(2)–Cl(2)	174.48(7)

reported the synthesis of diphosphine derivatives of thioureas, the latter showing that {Ph₂PN(Me)₂CS} can be formed from the reaction of *N,N'*-dimethylthiourea and two equivalents of chlorodiphenylphosphine. We have found that the analogous reaction involving *N,N'*-diethylthiourea results in the ligand [Ph₂PN(Et)₂CS] **16**. Reports of metal complexes containing ligands of the type [Ph₂PN(R)₂CE] (E = O, S) are rare. Schmutzler and Gruber reported the synthesis of [Ph₂P–N(Me)₂CS] but did not describe any complexation chemistry for the ligand.²⁵

We have found that reaction of [Ph₂PN(Me)₂CS] with equimolar quantities of [PtCl₂(cod)] in thf fails to give the expected *P,P'* chelate system and instead proceeds according to eqn. (7)



with P–N bond cleavage, to give the novel five-membered heterocycle **17**. The sulfur containing system probably behaves differently to **1** or **2** because of the tendency of the S atom to coordinate the metal centre. We envisage an intermediate containing a five-membered PtPNC(S) ring with the pendant N(Me)PPh₂ group undergoing P–N bond cleavage after the coordination is complete though we have no clear evidence supporting this mechanism. Clearly, hydrolytic P–N cleavage at this stage would give rise to Ph₂P(O)H/[Ph₂PO][–] which has the opportunity to coordinate in a similar fashion to **11** and **12**. The fact that this is not observed may suggest that the cleavage in the formation of **11** and **12** may be ‘associative’ with the opportunity for the ligand to coordinate through two phosphorus and one nitrogen atom in that case.

The ³¹P-{¹H} NMR spectrum of **17** shows a singlet with satellites from coupling to ¹⁹⁵Pt. The product has a chemical shift of δ_p 78.3 and the magnitude of the coupling [¹J(¹⁹⁵Pt–³¹P) 3967 Hz] suggests a platinum(II) complex where phosphorus is *trans* to chloride.²⁵ FAB⁺ mass spectrometry failed to show the

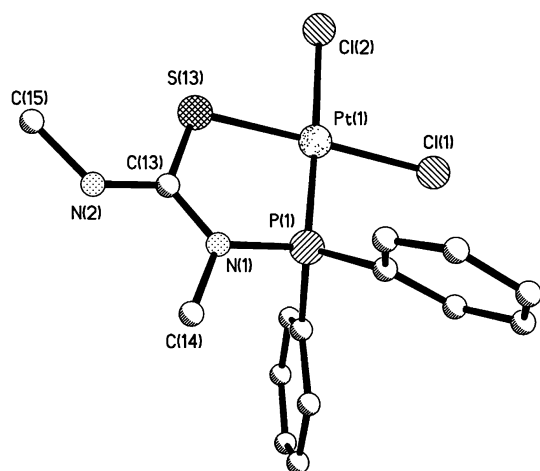


Fig. 5 Solid state structure of $[\text{PtCl}_2\{(\text{Ph}_2\text{PN}(\text{Me})\text{CSN}(\text{Me})\text{H}-P,S)\}]\cdot\text{dmsO}\cdot\text{CHCl}_3$ **17**.

Table 8 Selected bond lengths (Å) and bond angles (°) for **17**·dmsO·CHCl₃

Pt(1)–Cl(1)	2.324(4)	Cl(1)–Pt(1)–Cl(2)	91.10(14)
Pt(1)–Cl(2)	2.387(3)	P(1)–Pt(1)–S(13)	88.02(13)
Pt(1)–P(1)	2.188(3)	Pt(1)–P(1)–N(1)	106.8(4)
Pt(1)–S(13)	2.256(4)	P(1)–N(1)–C(13)	118.7(8)
P(1)–N(1)	1.739(10)	P(1)–N(1)–C(14)	120.7(9)
N(1)–C(14)	1.49(2)	N(1)–C(13)–S(13)	121.7(10)
N(1)–C(13)	1.34(2)	C(13)–S(13)–Pt(1)	104.0(5)
C(13)–S(13)	1.737(13)	C(13)–N(1)–C(14)	120.2(11)
C(13)–N(2)	1.34(2)	N(2)–C(13)–S(13)	119.3(10)
N(2)–C(15)	1.49(2)	C(15)–N(2)–C(13)	123.4(14)

expected parent-ion peak but did show a peak corresponding to **17** with the loss of a chloride ion (m/z 519 $[\text{M} - \text{Cl}]^+$). The solid state structure of **17**·dmsO·CHCl₃ (Fig. 5, Table 8) is a rare example of a fully characterised five-membered ‘true’ heterocycle (*i.e.* a heterocycle in which every ring atom is different), though there is a report of a related PtSNCP heterocycle.^{26,27} The X-ray structure of **17** reveals square planar coordination of the platinum with the five-membered PtPNCS ring being almost perfectly planar [maximum deviation from the PtPNCS plane is 0.11 Å for S(13), with N(2), C(14) and C(15) lying 0.05, 0.18 and –0.06 Å from this plane]. The bond lengths and angles within **17** are in the expected range. The Pt–Cl distances vary as a function of the *trans* element, within the five-membered PtPNCS heterocycle the P–N and C–N bonds are effectively single bonds whilst C(13)–S(13) is slightly longer than a formal C=S double bond.

Conclusion

Ligands of the type $\{\text{Ph}_2\text{PN}(\text{R})\}_2\text{C}=\text{E}$ (where R = Me or Et and E = O or S) can be readily synthesised *via* reactions of dialkylureas or thioureas with chlorodiphenylphosphine. Reactions of the compounds $[\text{Ph}_2\text{PN}(\text{Me})]_2\text{C}=\text{O}$ and $[\text{Ph}_2\text{PN}(\text{Et})]_2\text{C}=\text{O}$ with Pt(II), Pd(II), Mo(0) and Rh(III), results in the ligands acting as

P,P' chelates and formation of six-membered ring systems, while $[\text{Ph}_2\text{PN}(\text{Et})]_2\text{C}=\text{O}$ acts as a bridging ligand when reacted with Au(I). Different substituents on the nitrogen atoms appear to have little influence on bond lengths and angles within the metal complexes. The coordination chemistry of $[\text{Ph}_2\text{PN}(\text{Me})]_2\text{C}=\text{S}$ is less predictable and results in P–N bond cleavage and the formation of a five-membered heterocycle when reacted with Pd(II). Studies of the chemistry of these types of ligands are still far from extensive.

Acknowledgements

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