Journal of Organometallic Chemistry, 342 (1988) 269–280
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Unsymmetrically substituted dimethylplatinum(II) complexes

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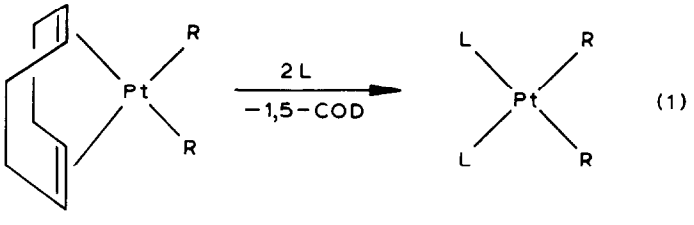
(Received August 11th, 1987)

Abstract

cis-(Dimethyl)(tri-*p*-tolylphosphine)(ligand)platinum(II) complexes (ligand = substituted pyridine or amine) have been prepared from $PtMe_2$(1,5-COD) (COD = cyclooctadiene), $Ptol_3$ (tol = tolyl) and the N-donor ligand. For ligand = 4-(5-phenyl-2-oxazolyl)pyridine the crystal and molecular structure has been determined: space group $R\bar{3}$, $a = b = 34.295(5)$, $c = 14.198(2)$ Å (−100 °C), γ 120 °, V 14459 Å^3, $Z = 18$. For 379 variables and 4977 reflections with $I > 2\sigma(I)$ $R = 0.034$, $R_w = 0.042$. Pt–C bond lengths are 2.082(7) (*trans* to P) and 2.059(8) Å (*trans* to N). Amine ligands are displaced by ethylene to form an unstable ethylene adduct.

Introduction

Ever since their discovery (diorgano)(diolefin)platinum(II) complexes **1** [1,2] have served as useful precursors to symmetrically substituted *cis*-(diorgano)(bisligand)-platinum(II) complexes **2** (eq. 1), where "ligand" is typically a phosphine, arsine, or stibine. In turn, *cis*-(diorgano)(bisligand)platinum(II) complexes **2** are convenient model systems for studying important organometallic reactions, in particular β-elimination (see ref. 3 and references therein), γ and δ C–H activation [4–7], and diaryl reductive elimination (see refs. 8, 9 and references therein).



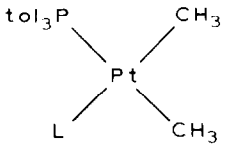
(1)

(1: R = CH_3) (2: L = PR_3, AsR_3)

* Contribution No. 3766.

0022-328X/88/$03.50

We were interested in preparing unsymmetrical complexes *cis*-(dialkyl)(ligand)-(ligand′)platinum(II), in particular dimethyl complexes where one of the supporting ligands is labile, and we explored methods for preparing such compounds starting from (dimethyl)(cyclooctadiene)platinum(II) (abbreviated as "$PtMe_2$(COD)" where COD = 1,5-cyclooctadiene) [1,2]. However, the COD ligand of $PtMe_2$(COD) is itself rather tightly bound, and its substitution normally requires either very strongly binding ligands, such as phosphines, which usually form the symmetrical bis-phosphine compound **2**, or forcing conditions that provide unreliable yields. Therefore we were surprised to discover a simple and convenient route for converting $PtMe_2$(COD) to $PtMe_2$(triarylphosphine)(ligand) compounds **3**, where "ligand" is a N-donor ligand (pyridine or amine) that does not ordinarily displace COD. In this article we describe the preparation and properties of several of these compounds, and include the crystal and molecular structure of a representative pyridine compound, **3c** (ligand = 4-(5-phenyl-2-oxazolyl)pyridine). We also describe the reaction of the amine compounds **3f, 3g, 3h** with ethylene to form the unusually labile and reactive ethylene adduct **4**.



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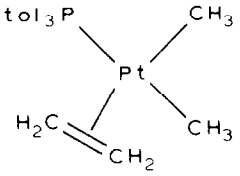


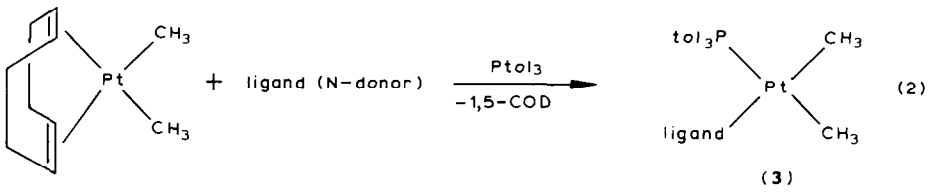
(4)

(**3a** L = pyridine;
3b L = 4-picoline;
3c L = 4(5-phenyl-2-oxazolyl)pyridine;
3d L = pyrazine;
3e L = 1/2(pyrazine);
3f L = piperidine;
3g L = neopentylamine;
3h L = NH_3)

Results

The synthesis of compounds **3** is outlined in eq. 2 (see Experimental Section). The success of this reaction arises from the nature of the $PtMe_2$(COD) starting material **1**: $PtMe_2$(COD) does not react at room temperature, or reacts only very slowly, with nitrogen-donor ligands [1,2,10,11]. However, when triarylphosphine is added slowly to a solution containing $PtMe_2$(COD) and excess N-donor ligand, a reaction ensues and the Me_2Pt(triarylphosphine)(ligand) complexes are formed in 60–90% yields, often analytically pure. We have used tri-*p*-tolylphosphine as the "triarylphosphine" ligand because it provides crystalline compounds with good stability and solubility properties, and has a simple ^1H NMR spectrum. Triphenylphosphine functions

equally well in the preparation of, for instance, analogous picoline and piperidine complexes. But when the reaction of eq. 2 is attempted using representative trialkylphosphines (trimethylphosphine, triethylphosphine) only symmetrical dimethyl(bisphosphine)Pt products are obtained (together with unreacted starting $PtMe_2(COD)$).

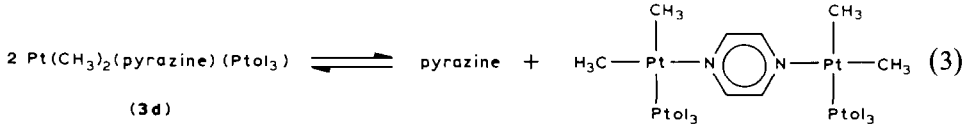


(2)

(3)

As can be seen from the list of compounds prepared by this method, the reaction succeeds for a variety of N-donor ligands. In the cases of weakly-binding arylamines (e.g. *p*-toluidine) and hindered trialkylamines and pyridines (e.g. triethylamine, 2,6-lutidine) we were unable to obtain satisfactory products. All complexes **3** undergo rapid substitution reactions with added phosphine ligands, which provides a very convenient method of preparing mixed-phosphine $PtMe_2(Ptol_3)$(phosphine′) compounds. For this reason triarylphosphine must be added slowly to the reaction mixture and any excess must be avoided. If excess triarylphosphine is added, or if the N-donor ligand is present in insufficient amounts (a two-fold excess is usually adequate), the desired product compound **3** will be contaminated with the bisphosphine compound $PtMe_2$(triarylphosphine)$_2$.

All compounds **3** are white crystalline solids (except for **3c** and **3e**, which are yellow), are indefinitely stable in the solid state at room temperature under a nitrogen atmosphere, and tolerate at least some exposure to air. They are likewise indefinitely stable in solution (benzene, dichloromethane) under a nitrogen atmosphere, except for those compounds where the ligand has several ligating N donor sites (compounds **3c, 3d**). In these cases, an equilibrium is established with a dimeric compound and free ligand, illustrated in eq. 3 for the pyrazine compound **3d**. We prepared the dimeric pyrazine compound **3e** by using one-half an equivalent of pyrazine per platinum in the synthetic reaction (eq. 2) but it was contaminated by a mixture of compounds, including $PtMe_2(Ptol_3)_2$ and compound **3d**. A spectroscopically pure sample of the dimeric pyrazine-bridged compound **3e** was obtained by reacting the ammonia compound **3h** with one-half equivalent of pyrazine and forcing the complete displacement of NH_3 with an ethylene purge (see below).



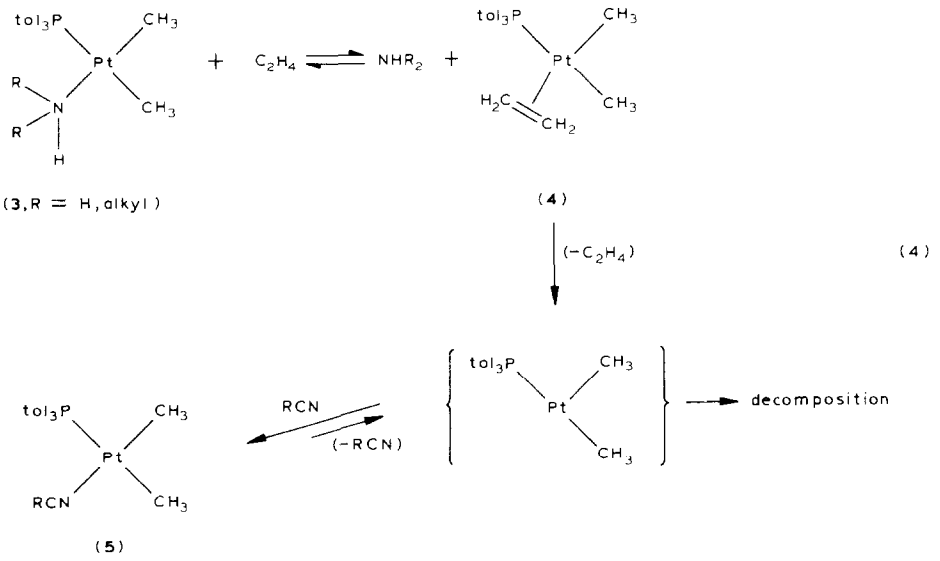
(3d)

(3e)

(3)

Amine ligands in compounds **3f, 3g, 3h** are bound less strongly than non-bridging pyridine ligands, and are partially displaced by ethylene to establish equilibrium with the ethylene complex **4** (eq. 4). The reaction is driven to completion by removing the released amine ligand, which has been accomplished by adding phenyl

isocyanate to the reaction mixture of compound **3g** and ethylene, and in the case of the ammonia complex **3h** by continued purging with ethylene. The ethylene complex **4** is indefinitely stable in benzene solution at room temperature under an atmosphere of ethylene but when the excess ethylene is removed (vacuum or by purging with nitrogen) compound **4** decomposes, forming an uncharacterized dark colloidal material together with $PtMe_2(Ptol_3)_2$, C_2H_4, CH_4, and traces of C_2H_6 (^1H NMR). In acetonitrile solution the decomposition is suppressed, presumably by formation of an acetonitrile compound $PtMe_2$(acetonitrile)($Ptol_3$) (**5**) (eq. 4). This putative acetonitrile compound is stable only in acetonitrile solution and decomposes upon attempted isolation.



To our knowledge, dimethylplatinum(II) complexes with mixed phosphine-pyridine or phosphine-amine supporting ligands have not been structurally characterized, and we were interested in the structural details of a representative compound. Satisfactory single crystals of the 4-(5-phenyl-2-oxazolyl)pyridyl compound **3c** were obtained and its structure was determined by X-ray diffraction. A perspective drawing of the molecule is shown in Fig. 1, with bond distances and angles in Tables 1 and 2. As expected, the coordination plane about the platinum atom is planar and nominally square but with some deviation from 90° interligand angles. The most interesting aspect of the structure is the difference in Pt–C bond distances; the Pt–C bond *trans* to the phosphine ligand (Pt–C(1), 2.082(7) Å) is 0.02 Å longer than the Pt–C bond *trans* to the 4-substituted pyridine ligand (Pt–C(2), 2.059(8) Å). While this difference is slight and only marginally significant it is consistent with our expectation that the pyridine ligand exerts a smaller *trans* influence than the phosphine ligand. Both Pt–C bonds are substantially shorter than those of $Pt(CH_3)_2(P(C_6H_5)_2CH_3)_2$ [12] (2.122(6), 2.119(5) Å) but the Pt–C(1) bond length is identical to the value reported for $Pt(CH_3)$(C-tripyrazolylmethane)($P(C_6H_5)_3$)(pyridine) [13] (2.083(9) Å).

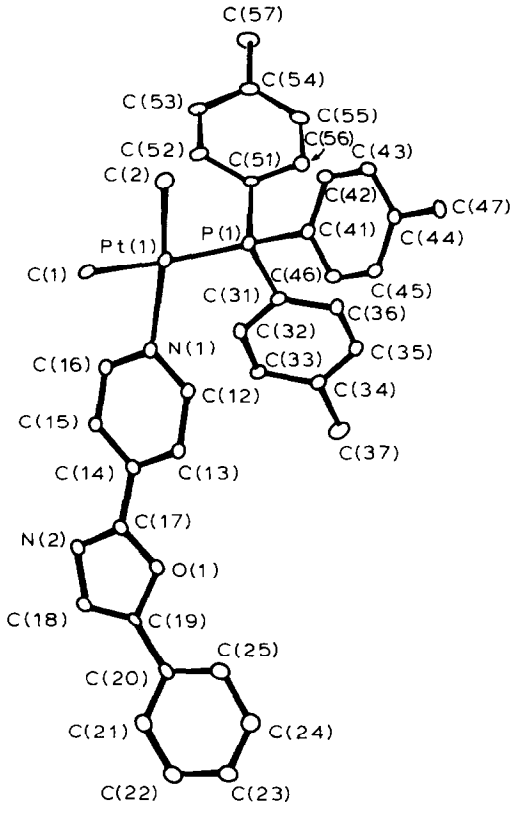


Fig. 1. Perspective view of $PtMe_2$(4-(5-phenyl-2-oxazolyl)pyridine)($Ptol_3$), compound **3c**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Interatomic distances (Å)

Pt(1)–P(1)	2.286(2)	C(23)–C(24)	1.361(11)
Pt(1)–N(1)	2.122(6)	C(24)–C(25)	1.376(12)
Pt(1)–C(1)	2.082(7)	C(31)–C(32)	1.381(9)
Pt(1)–C(2)	2.059(8)	C(31)–C(36)	1.397(9)
P(1)–C(31)	1.830(7)	C(32)–C(33)	1.391(9)
P(1)–C(41)	1.824(7)	C(33)–C(34)	1.389(10)
P(1)–C(51)	1.827(7)	C(34)–C(35)	1.403(10)
O(1)–C(17)	1.361(9)	C(34)–C(37)	1.497(10)
O(1)–C(19)	1.380(8)	C(35)–C(36)	1.398(10)
N(1)–C(12)	1.350(8)	C(41)–C(42)	1.387(9)
N(1)–C(16)	1.359(9)	C(41)–C(46)	1.398(9)
N(2)–C(17)	1.292(9)	C(42)–C(43)	1.394(10)
N(2)–C(18)	1.387(9)	C(43)–C(44)	1.394(10)
C(12)–C(13)	1.388(9)	C(44)–C(45)	1.392(10)
C(13)–C(14)	1.394(9)	C(44)–C(47)	1.513(10)
C(14)–C(15)	1.394(10)	C(45)–C(46)	1.383(10)
C(14)–C(17)	1.463(10)	C(51)–C(52)	1.385(9)
C(15)–C(16)	1.366(10)	C(51)–C(56)	1.401(10)
C(18)–C(19)	1.347(10)	C(52)–C(53)	1.398(10)
C(19)–C(20)	1.459(10)	C(53)–C(54)	1.385(11)
C(20)–C(21)	1.367(10)	C(54)–C(55)	1.397(11)
C(20)–C(25)	1.384(11)	C(54)–C(57)	1.496(10)
C(21)–C(22)	1.392(11)	C(55)–C(56)	1.387(10)
C(22)–C(23)	1.364(11)		

Table 2

Intramolecular angles (°)

P(1)–Pt(1)–N(1)	98.8(2)	C(14)–C(15)–C(16)	120.2(7)
P(1)–Pt(1)–C(1)	175.5(2)	C(18)–C(19)–C(20)	133.9(6)
P(1)–Pt(1)–C(2)	89.6(2)	C(19)–C(20)–C(21)	119.3(7)
N(1)–Pt(1)–C(1)	85.5(3)	C(19)–C(20)–C(25)	121.7(6)
N(1)–Pt(1)–C(2)	171.5(3)	C(21)–C(20)–C(25)	119.0(7)
C(1)–Pt(1)–C(2)	86.1(3)	C(20)–C(21)–C(22)	120.9(7)
Pt(1)–P(1)–C(31)	118.8(2)	C(21)–C(22)–C(23)	119.4(7)
Pt(1)–P(1)–C(41)	111.7(2)	C(22)–C(23)–C(24)	119.8(8)
Pt(1)–P(1)–C(51)	116.2(2)	C(23)–C(24)–C(25)	121.3(8)
C(31)–P(1)–C(41)	103.5(3)	C(20)–C(25)–C(24)	119.6(8)
C(31)–P(1)–C(51)	100.7(3)	C(32)–C(31)–C(36)	117.7(6)
C(41)–P(1)–C(51)	103.9(3)	C(31)–C(32)–C(33)	121.8(6)
C(17)–O(1)–C(19)	104.0(5)	C(32)–C(33)–C(34)	121.0(6)
Pt(1)–N(1)–C(12)	121.3(5)	C(33)–C(34)–C(35)	117.6(6)
Pt(1)–N(1)–C(16)	121.3(5)	C(33)–C(34)–C(37)	122.4(7)
C(12)–N(1)–C(16)	117.3(6)	C(35)–C(34)–C(37)	120.0(7)
C(17)–N(2)–C(18)	103.7(6)	C(34)–C(35)–C(36)	120.9(7)
P(1)–C(31)–C(32)	118.6(5)	C(31)–C(36)–C(35)	120.9(7)
P(1)–C(31)–C(36)	123.5(5)	C(42)–C(41)–C(46)	117.7(6)
P(1)–C(41)–C(42)	122.9(5)	C(41)–C(42)–C(43)	121.1(6)
P(1)–C(41)–C(46)	119.2(5)	C(42)–C(43)–C(44)	121.1(6)
P(1)–C(51)–C(52)	119.8(5)	C(43)–C(44)–C(45)	117.5(6)
P(1)–C(51)–C(56)	121.9(5)	C(43)–C(44)–C(47)	121.3(6)
O(1)–C(17)–N(2)	114.8(6)	C(45)–C(44)–C(47)	121.1(6)
O(1)–C(17)–C(14)	118.1(6)	C(44)–C(45)–C(46)	121.5(6)
O(1)–C(19)–C(18)	107.1(6)	C(41)–C(46)–C(45)	121.1(6)
O(1)–C(19)–C(20)	118.8(6)	C(52)–C(51)–C(56)	118.1(6)
N(1)–C(12)–C(13)	122.9(6)	C(51)–C(52)–C(53)	120.6(7)
N(1)–C(16)–C(15)	122.7(6)	C(52)–C(53)–C(54)	122.2(7)
N(2)–C(17)–C(14)	127.1(7)	C(53)–C(54)–C(55)	116.5(7)
N(2)–C(18)–C(19)	110.3(6)	C(53)–C(54)–C(57)	121.5(7)
C(12)–C(13)–C(14)	119.2(6)	C(55)–C(54)–C(57)	122.0(8)
C(13)–C(14)–C(15)	117.6(6)	C(54)–C(55)–C(56)	122.2(7)
C(13)–C(14)–C(17)	122.3(6)	C(51)–C(56)–C(55)	120.4(7)
C(15)–C(14)–C(17)	120.1(7)		

Discussion

While $PtMe_2(COD)$ and other $Pt(alkyl)_2(COD)$ compounds are valuable starting materials for formation of $Pt(alkyl)_2(ligand)_2$ complexes, the ligands that have been used commonly are strongly-binding "soft" ligands such as phosphines, isocyanides or CO. "Harder" N-donor ligands do not react readily with $PtMe_2(COD)$ and the examples that have been reported have either required lengthy reaction times (bipyridine, 3 weeks [10]) or forcing reaction conditions (pyridine, at reflux [1]). Indeed, the success of our synthetic reaction (eq. 2) depends on the inability of the N-donor ligand to displace COD: There is no reaction between molecules of $PtMe_2(COD)$ and the N-donor compound, until a molecule of triarylphosphine binds to the Pt center and displaces at least one double bond of the COD ligand; whereupon the N-donor compound (which is present in excess) does bind to the platinum center to form the final compound **3**.

The difficulty with which N-donor ligands displace COD from $PtMe_2$(COD) is thought to be a consequence of the stability of the Pt-COD entity [14,15]. After we had begun our studies on $PtMe_2$(COD) the work of Appleton et al. [14,15] documented the significantly lesser stability of the Pt–NBD (NBD = norbornadiene) entity and the ability of pyridine and amines to displace NBD from $PtMe_2$(NBD) to form $PtMe_2$(N-ligand)$_2$ complexes. These $PtMe_2$(N-ligand)$_2$ compounds are somewhat less stable than the $PtMe_2(Ptol_3)$(N-ligand) complexes **3** described herein and provide yet additional examples of the stabilizing influence exerted by phosphine ligands.

The N-donor ligands of compounds **3** are all labile and are replaced at room temperature by phosphine ligands, without decomposition of the organoplatinum entity and without scrambling of the phosphine ligands. But in the case where the ligand is very labile, i.e. ethylene and acetonitrile, the respective compounds **4** and **5** become unstable and the organoplatinum entity decomposes. Probably, loss of the weakly-bound ligand forms a very reactive 3-coordinate species. Such species have been proposed as participants in ligand substitution reactions and alkyl/halogen exchange reactions [see for example ref. 16], β-elimination [2,17], γ- and δ-elimination [4–7] and dialkyl reductive elimination [18 and references therein]. (Ligand dissociation may be a fairly general mechanism for reductive elimination, as for example in the work of Milstein [19]). Thus it is no surprise that "$PtMe_2(Ptol_3)$", formed by ligand loss from compound **4**, decomposes, although the exact pathway(s) is (are) not straightforward (see below). As an aside, the ethylene in compound **4** appears to be more labile than usual for platinum(II) compounds (see for instance [20] and references therein), even compared with other *cis*- or *trans*-(methyl)(ethylene)platinum(II) compounds [21,22,23,24]. But compound **4** is, to our knowledge, the only example of an (ethylene)platinum(II) compound having both *cis*- and *trans*-methyl groups, and their combined influence must be responsible for the unusual ethylene lability.

The decomposition of compound 4

The major products observed when a sample of compound **4** decomposed in C_6D_6 solution in an evacuated, sealed NMR tube (see Experimental Section) are $PtMe_2(Ptol_3)_2$, CH_4, and C_2H_4. Also present is a dark colloidal material of unknown composition. Only trace amounts of ethane, ca. 10% of the amount of methane present, were identified in the NMR solution. One complicating factor is that a sealed reaction vessel is needed in order to retain and detect gaseous decomposition products, but ethylene necessarily accumulates as compound **4** decomposes, and ethylene accumulation inhibits further decomposition.

A detailed study of the mechanism has not been possible but we note the following observations: (1) The amount of $PtMe_2(Ptol_3)_2$ formed is approximately half (within 10%) of the amount of compound **4** initially present. Therefore at least 80% of the tri-*p*-tolylphosphine is accounted for. In addition, any proposed mechanism must account for this facile phosphine redistribution, which does not occur for any of the other compounds. (2) When doubly-$^{13}CH_3$-labeled compound **4** decomposed under comparable conditions no ^{13}C-ethylene was detected. Therefore the ethylene that is observed is just the ethylene initially present in compound **4**, and does not arise from coupling reactions between the Pt–CH_3 groups. The methane observed is $^{13}CH_4$. (3) When the decomposition of compound **4** is carried out in the

presence of COD, the course of the reaction is altered; little if any colloidal material or methane is formed and $PtMe_2(Ptol_3)_2$ and $PtMe_2$(COD) are formed in good yield (> 85%).

From these observations we propose a mechanism in which the first step is loss of ethylene to form a reactive 3-coordinate compound. In some manner not presently understood this fragment transfers its remaining triarylphosphine ligand to another platinum center, perhaps an unreacted molecule of compound **4**. (Bimolecular intermediates are quite possible and have precedent in other dimeric methylplatinum compounds, in which a nominally 3-coordinate platinum compound binds to a nominally 4-coordinate platinum center [25,26].) The resulting hypothetical "$PtMe_2$" fragment (undoubtedly solvated) is trapped by COD, if present, to form $PtMe_2$(COD). Otherwise, "$PtMe_2$" decomposes rapidly, primarily evolving methane and forming some insoluble platinum-containing material. Decomposition reactions of other methylplatinum compounds [27,28] provide methane, either from α elimination or from Pt–CH_3 bond homolysis.

Summary and conclusion

The reaction of eq. 2 is a convenient route to unsymmetrically substituted compounds Me_2Pt(triarylphosphine)(ligand) (**3**) free of symmetrically-substituted byproducts. While certain unsymmetrically-substituted platinum compounds are readily available by other routes, such as cleavage of bridged dimers by added ligand, the reactions and compounds we describe are a useful complement to the organoplatinum compounds already reported in the literature, and provide access to many other unsymmetrical compounds.

The success of this synthetic method depends upon the details of COD substitution. Clearly the addition of one phosphine ligand makes the COD ligand much more labile, and susceptible to rapid substitution by pyridine and amine ligands that cannot ordinarily displace COD. Given the probable participation of the $PtMe_2(Ptol_3)$ fragment in eq. 4, we suspect that the COD ligand is entirely displaced by the phosphine ligand, allowing the pyridine or amine ligand to bind without difficulty.

Experimental

All reactions and manipulations were carried out under dinitrogen using dried, degassed solvents, and at room temperature unless otherwise noted. NMR spectra were recorded at ambient probe temperature using a GE/Nicolet QE-300 spectrometer. NMR chemical shift data are reported in ppm downfield from external Me_4Si, and coupling constants in Hz. The NMR data for compounds **3** are summarized in Table 3. $PtMe_2$(COD) was prepared by a modification of the literature method [2], and $Ptol_3$ and all nitrogen-donor ligands were obtained commercially. C, H, N analyses were performed by Galbraith Laboratories.

All compounds **3** were prepared in a similar manner and we describe two examples. In a typical reaction 0.22 g $PtMe_2$(COD) and 0.25 g 4-picoline dissolved in 10 ml hexane and a solution of 0.20 g $Ptol_3$ in 25 ml hexane was added dropwise over 30 min. The mixture was stirred an additional 30 min and filtered, yielding 0.32 g white solid (78%). Anal. Found: C, 55.84, H, 5.40. $PtMe_2$(4-picoline)($Ptol_3$) (**3b**),

Table 3

NMR data [a]

Compound (solvent)	Pt–CH_3 [b]	$Ptol_3$ [c]	Other
$PtMe_2$(pyridine)($Ptol_3$) (**3a**)	0.43 (8.0, 69.8)	2.34(s)	6.92(m), 2H;
(CD_2Cl_2)	0.46 (7.9, 85.0)	7.07(d), 7.33(t,8.5)	7.46(tt,7.5,2),1H;
			8.32(d,7,of t,2), 2H
$PtMe_2$(4-picoline)($Ptol_3$) (**3b**)	0.40 (7.8, 68.8)	2.34(s)	2.20(s)
(CD_2Cl_2)	0.42 (7.8, 84.4)	7.08(d), 7.32(t,8)	6.73(d), 8.12(d,5.7)
$PtMe_2$(4-(5-phenyl-2-oxazolyl)-			
pyridine)($Ptol_3$) (**3c**)	0.50 (7.9, [d])	2.33(s)	7.5(m), 5H;
(CD_2Cl_2)	0.54 (8.3, [d])	7.10(d), 7.36(t,8)	7.77(d), 8.44(d,7)
$PtMe_2$(pyrazine)($Ptol_3$) (**3d**)	0.43 (7.3, 69.2)	2.35(s)	8.14(m), 2H;
(CD_2Cl_2)	0.54 (8.2, 85.7)	7.10(d), 7.34(t,9)	8.26(m), 2H
[$PtMe_2$($Ptol_3$)]$_2$(pyrazine) (**3e**)	0.39 (7.6, 72)	2.37(s)	7.84(s)
(CD_2Cl_2)	0.52 (8.1, 85)	7.10(d), 7.28(t,9)	
$PtMe_2$(piperidine)($Ptol_3$) (**3f**)	0.28 (7, 85)	2.40(s)	0.65(br),2H;
(CD_2Cl_2)	0.46 (8, 67)	7.25(d), 7.54(t,8)	1.27(m), 1H;
			1.41(br), 3H;
			1.90(br), 1H;
			2.70(m), 4H
$PtMe_2$(neopentylamine)($Ptol_3$) (**3g**)	0.33 (8, 88)	2.38(s)	0.57(s), 9H;
(CD_2Cl_2)	0.37 (8, 68)	7.22(d), 7.48(t,8)	2.07(br s), 4H
$PtMe_2(NH_3)$($Ptol_3$) (**3h**)	0.36 (7.8, 66.4)	2.39(s)	1.72 (pseudo t, 12)
(CD_2Cl_2)	0.37 (7.6, 88.8)	7.22(d), 7.46(t,8)	
$PtMe_2(C_2H_4)$($Ptol_3$) (**4**)	1.21 (7.6, 66.7)	1.95(s)	3.71 (J(H–P) 3.2,
(C_6D_6)	1.56 (7.6, 85.3)	6.86(d), 7.57(t,8.5)	J(H–Pt) 37.3)
$PtMe_2(CD_3CN)$($Ptol_3$) (**5**)	0.87 (7.8, 90.0)	2.03(s)	
(C_6D_6/CD_3CN)	1.10 (7.8, 67.5)	6.91(d), 7.55(t,8)	

[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz in parentheses. [b] First number in parentheses: J(H–P); second number: J(H–^{195}Pt). [c] Aryl signals of $Ptol_3$ occasionally show additional fine splitting. [d] Obscured by signals from dimeric compound.

Table 4

Crystallographic data of compound **3c**

Complex	$PtMe_2$(4-(5-phenyl-2-oxazolyl)pyridine)($Ptol_3$)
Formula	$C_{37}H_{37}N_2O_1P_1Pt_1$
Formula weight	751.78
Space group	$R\bar{3}$ (no. 148)
a (Å)	34.295(5)
b (Å)	34.295(5)
c (Å)	14.198(2)
γ (deg.)	120
V (Å^3)	14459
Z	18
Temp. (° C)	−100
Radiation	Mo-K_α 0.71069 Å
2-θ limits (deg)	4.0–55.0
Absorption coefficient	44.882 cm^{-1}
Absorption correction	Calculated
Total no. of unique observations	7383
Data used in refinement,	
$F > 2\sigma(F)$	4977
Final no. of variables	379
R, R_w	0.034, 0.042

$C_{29}H_{34}NPPt$ calc.: C, 55.94; H, 5.50%. The ammonia complex **3h** was prepared by dropwise addition of an ether solution of $Ptol_3$ (0.64 g in 15 ml) to an ether solution of $PtMe_2(COD)$ (0.70 g in 50 ml) while passing ammonia slowly through the reaction mixture. The mixture was filtered after concentrating to 20 ml, yielding 0.95 g white solid (83%). Anal. Found: C, 50.48, H, 5.40, N, 2.61%. $PtMe_2(NH_3)(Ptol_3)$, $C_{23}H_{30}NPPt$ calc.: C, 50.54, H, 5.53. N, 2.56%. Similarly

Table 5

Fractional coordinates ($\times 10^5$) and isotropic thermal parameters

Atom	x	y	z	B_{iso}
Pt(1)	547.6(1)	4739.8(1)	3950.8(2)	1.6(1)′
P(1)	1211(1)	5375(1)	4309(1)	1.6(1)′
O(1)	−300(2)	4205(2)	8657(3)	2.1(2)′
N(1)	330(2)	4500(2)	5339(4)	1.9(2)′
N(2)	−271(2)	3578(2)	8379(4)	2.5(2)′
C(1)	−53(2)	4183(3)	3520(5)	2.7(3)′
C(2)	663(3)	4904(3)	2544(5)	2.7(3)′
C(12)	209(2)	4725(2)	5944(5)	1.9(2)′
C(13)	39(2)	4565(2)	6836(5)	2.0(2)′
C(14)	−3(2)	4160(2)	7138(5)	1.9(2)′
C(15)	126(2)	3931(2)	6513(5)	2.2(3)′
C(16)	282(2)	4102(2)	5637(5)	2.2(2)′
C(17)	−191(2)	3964(2)	8058(5)	2.3(2)′
C(18)	−454(2)	3554(3)	9262(5)	2.5(3)′
C(19)	−469(2)	3932(2)	9439(5)	1.9(2)′
C(20)	−591(2)	4103(2)	10263(5)	2.1(2)′
C(21)	−761(3)	3836(3)	11042(5)	2.7(3)′
C(22)	−869(3)	3992(3)	11849(5)	2.9(3)′
C(23)	−792(3)	4423(3)	11871(6)	3.1(3)′
C(24)	−630(3)	4687(3)	11091(6)	3.9(4)′
C(25)	−533(3)	4533(3)	10282(6)	3.4(3)′
C(31)	1406(2)	5470(2)	5533(4)	1.7(2)′
C(32)	1330(2)	5105(2)	6074(5)	1.8(2)′
C(33)	1484(2)	5153(2)	6997(5)	2.1(2)′
C(34)	1724(3)	5576(3)	7411(5)	2.3(3)′
C(35)	1818(3)	5951(3)	6855(5)	2.6(3)′
C(36)	1653(3)	5898(2)	5935(5)	2.3(3)′
C(37)	1880(3)	5639(3)	8413(5)	3.2(3)′
C(41)	1198(2)	5885(2)	4007(5)	1.8(2)′
C(42)	1375(2)	6119(2)	3174(5)	2.1(3)′
C(43)	1327(2)	6487(2)	2935(5)	2.2(3)′
C(44)	1108(2)	6638(2)	3535(5)	2.0(2)′
C(45)	930(2)	6400(2)	4367(5)	2.1(2)′
C(46)	968(2)	6028(2)	4595(5)	1.9(2)′
C(47)	1051(3)	7034(2)	3275(5)	2.5(3)′
C(51)	1712(2)	5442(2)	3707(4)	1.8(2)′
C(52)	1689(2)	5088(2)	3194(5)	2.1(3)′
C(53)	2076(3)	5121(3)	2790(5)	2.5(3)′
C(54)	2495(3)	5506(3)	2874(5)	2.5(3)′
C(55)	2512(3)	5860(3)	3391(5)	2.8(3)′
C(56)	2133(2)	5833(3)	3804(5)	2.3(3)′
C(57)	2906(3)	5536(3)	2434(6)	3.6(4)′

satisfactory C, H, N, analyses were obtained for compounds **3a** (Found C, 55.16, H, 5.34, N, 2.27. $C_{28}H_{32}NPPt$ calc.: C, 55.26, H, 5.30, N, 2.30%), **3f** (Found C, 54.74, H, 6.03, N, 2.28. $C_{28}H_{38}NPPt$ calc.: C, 54.71, H, 6.23, N, 2.28%) and **3g** (Found: C, 54.53, H, 6.75, N, 2.14. $C_{28}H_{40}NPPt$ calc.: C, 54.53, H, 6.54, N, 2.27%). Analytically pure samples of compounds **3c**, **3d**, **3e** were not obtained, owing to the monomer–dimer equilibrium of eq. 3.

To characterize the decomposition reaction, 0.02 g of compound **3h** was suspended in C_6D_6 in a NMR tube and ethylene was passed through the mixture for 4 h, during which time the material all dissolved. After brief purging with dinitrogen the tube was sealed under vacuum. NMR analysis of the clear solution showed the presence of ethylene compound **4** (ca. 90%) with a small amount (ca. 10%) of the bisphosphine compound $PtMe_2(Ptol_3)_2$.

After the sealed tube was heated for 21 h at 45 °C the dark mixture contained unreacted ethylene compound **4** (45%), bisphosphine compound $PtMe_2(Ptol_3)_2$ (45%), uncharacterized phosphine-containing compounds (10%), together with CH_4 (NMR 0.12 ppm), C_2H_4 (NMR 5.20 ppm), and a trace of C_2H_6 (NMR 0.74 ppm). Comparable decomposition of solutions of compound **4** occurred within 5 h at room temperature in a vessel open to a dinitrogen atmosphere, and within 1 h under a dinitrogen purge.

X-Ray structural determination

A pure single crystal of compound **3c** was cleaved from a larger mass of irregular yellow blocks, obtained by crystallizing impure compound **3c** from dichloromethane/pentane solution. X-ray data were collected using methods standard in our laboratory (see ref. 29). Crystallographic data are summarized in Table 4. The structure was solved by direct methods, hydrogen atoms were placed at calculated positions with an isotropic thermal parameter of 2.5, and refinement was uneventful, converging to $R = 0.034$, $R_w = 0.042$. Final positional and equivalent isotropic thermal parameters are listed in Table 5. Derived distances and angles are listed in Tables 1 and 2. Anisotropic thermal parameters (Table 6), hydrogen atom positions (Table 7), and observed and calculated structure factors (Table 8) are available from the authors.

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