

8. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions

Part XIV¹⁾

Some Complexes of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene with Platinum(0) and their Reactivities

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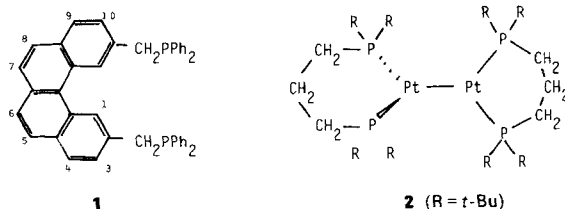
Summary

The ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) has been used to prepare complexes of the type [PtL(**1**)] (L = C₂H₄, CH₂=CH–CO₂Me, PhC≡CPh, MeC≡CMe, MeO₂CC≡CCO₂Me, (i-Pr)O₂CC≡CCO₂(i-Pr), Ph₃P and CO). It is shown that these complexes are less labile than the corresponding species [PtL(Ph₃P)₂]. The preparation of complexes *trans*-[PtX(R)(**1**)] by oxidative addition of RX (RX = PhCH₂Br and MeI) to [Pt(C₂H₄)(**1**)] is described. The isolation of [PtO₂(CH₃)₂CO(**1**)] is also reported.

Introduction. – The coordination chemistry of Pt(0) has been the object of increasing interest in recent years [2]. The discovery of a convenient method of preparation of the complex [Pt(COD)₂] (COD = 1,5-cyclooctadiene) [3] has opened up several new fields of research [4]. Furthermore, the need for efficient catalytic systems in several areas, *e.g.*, the *Water-Gas Shift* and *Fischer-Tropsch* reactions [5] and solar energy conversion, has prompted the study of the interactions of various low-valent metal centres with small molecules such as H₂, O₂, CO, CO₂, H₂O and CH₃OH.

Phosphines have played a significant role in this development and the study of the reactions of small molecules with species such as [PtL₂] (L = PCy₃, P(*t*-Bu)₃, *etc.*) [6] has stressed the importance of the phosphine on the reactivity of such species. During the study of the coordinating properties of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) [7], a molecule designed to preferentially span *trans*-positions, we have prepared and report here a number of complexes of Pt(0) containing this ligand.

¹⁾ Part XIII: see [1].



An additional reason for this study was the search for alternative routes to complexes of the type *trans*-[PtX(R)(1)] which might be obtainable by the oxidative addition of RX to complexes of Pt(0)-containing ligand **1**.

Results and Discussion. – The most desirable starting material for the preparation of a series of complexes of the type [PtL(1)] (L = monodentate ligand), would have been [Pt(1)]. This species would have been analogous to complexes of the type [Pt(PR₃)₂] which have an extensive chemistry and are related to compounds such as **2** having Pt-Pt bonds [8].

Treatment of [Pt(COD)₂] with **1** in toluene resulted in the formation of a sparingly soluble orange material which could not be characterized. Its ³¹P-NMR spectrum, in CD₂Cl₂, showed only one signal at 33.15 ppm without ¹⁹⁵Pt-satellites even at –78°. In this context it is noteworthy that species [Pt(PR₃)₂] are well-known for phosphines with bulky substituents, *i.e.*, R = Cy and *t*-Bu [9], but that the isolation of [Pt(PPh₃)₂] has been problematic as a result of low stability and high reactivity [10].

At the time this study was started it was known that three-coordinate complexes of the type [MX(1)] (M = Cu, Ag and Au) could be formed [11] and that the P-Cu-P bond angle in [CuCl(1)] was 132° [12]. Thus, it was uncertain whether ligand **1** would give stable complexes of the type [PtL(1)] as the P-Pt-P bond angles in the complexes [PtL(PR₃)₂] fall around 120° [13]. More recently it has become apparent that ligand **1** is capable of tolerating highly strained conformations in order to form complexes with bond angles which do not significantly depart from the electronically preferred values [7]. However, it was anticipated that the preparation of three-coordinate Pt(0)-complexes with ligand **1** would require modifications of the standard procedures used for the preparation of analogous species with monodentate phosphines [13].

The reaction of ligand **1** with [Pt(C₂H₄)₃], generated *in situ* from [Pt(COD)₂] [3], led to the formation of [Pt(C₂H₄)₄(1)]_x (x = 1 or 2, **3**) as a sparingly soluble white solid. Molecular-weight determinations did not discriminate between a mononuclear (**3a**) or binuclear formulation (**3b**) presumably owing to a combination of low solubility, dissociation and air sensitivity when in solution. Despite its poor solubility this complex proved to be a suitable starting material for the preparation of other Pt(0)-complexes.

The mother liquors from the preparation of **3** yield also small, variable amounts of [Pt₂(C₂H₄)₄(1)] which has been assigned structure **4**. The coordinated ethylenes of **4** give rise to a single ¹H-NMR resonance (in CD₂Cl₂) at 2.41 δ (*J*(Pt,H) = 59 Hz) and a single ¹³C-NMR resonance at 47.14 δ (*J*(Pt,C) = 72 Hz; *J*(P,C) = 1.5 Hz). These values are consistent with fast rotation of the ethylenes on the NMR time-scale and are fully compatible with published data on related mononuclear Pt-systems [14].

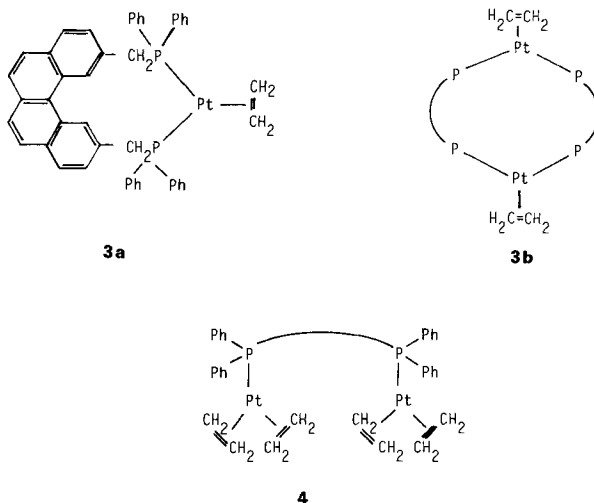


Table 1. ^{31}P -NMR Data for Pt-Complexes (in the compounds containing inequivalent P-atoms these have been arbitrarily denoted as P_a and P_b)

Compound	Solvent [ppm]	$\delta(\text{P}_a)$ [Hz]	$^1J(\text{Pt}, \text{P}_a)$ [ppm]	$\delta(\text{P}_b)$ [Hz]	$^1J(\text{Pt}, \text{P}_b)$ [Hz]	$^2J(\text{P}_a, \text{P}_b)$
3 $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{1})]$	CH_2Cl_2	24.9	3374			
4 $[\text{Pt}_2(\text{C}_2\text{H}_4)_4(\mathbf{1})]$	toluene	17.7	3397			
5 $[\text{Pt}(\text{CH}_2=\text{CHCO}_2\text{Me})(\mathbf{1})]$	CDCl_3^a	24.2	4181	19.9	3532	50
6 $[\text{Pt}(\text{PhC}\equiv\text{CPh})(\mathbf{1})]$	CDCl_3	16.9	3511			
7 $[\text{Pt}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\mathbf{1})]$	CDCl_3	15.5	3692			
8 $[\text{Pt}(\text{PPh}_3)(\mathbf{1})]$	toluene	39.8 ^b	4506	48.7 ^c	4465	143
9 $[\text{Pt}(\text{CO})(\mathbf{1})]$	toluene ^d	-4.0	3347			
10 $[\text{Pt}(\text{O}_2)(\mathbf{1})]$	CH_2Cl_2	8.4	4099			
$[\text{Pt}(\text{O}_2)(\text{PPh}_3)_2]$	CDCl_3	14.8	4084			
11 $[\text{Pt}(\text{O}_2\text{CMe}_2\text{O})(\mathbf{1})]$	CDCl_3	2.3	3491	0.9	3355	176
13 $[\text{Pt}(\text{Me})(\mathbf{1})]$	CDCl_3	19.1	3014			
14 $[\text{PtBr}(\text{CH}_2\text{Ph})(\mathbf{1})]$	^e	16.3	3208			
15 $[\text{Pt}(\text{PhC}\equiv\text{CMe})(\mathbf{1})]$	CDCl_3	17.0	3515			
16 $[\text{Pt}(\text{DIA})(\mathbf{1})]^f$	C_6D_6	15.4	3684			

^a) At 0° . ^b) P-resonances of **1**. ^c) P-resonance of PPh_3 . ^d) At -23° . ^e) $\text{CH}_2\text{Cl}_2/(\text{D}_6)\text{Acetone}$ (4:1). ^f) $\text{DIA} = (\text{i-Pr})\text{O}_2\text{CC}\equiv\text{CCO}_2(\text{i-Pr})$.

The olefin-exchange reactions of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{Ph}_3\text{P})_2]$ are well-known [15], and we found that $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{1})]_x$ reacted under mild conditions with an excess of methyl acrylate to give $[\text{Pt}(\text{CH}_2=\text{CHCO}_2\text{Me})(\mathbf{1})]$ (**5**) which is quite soluble in many organic solvents and not particularly sensitive to atmospheric degradation when in solution where it is present as a monomer. Complex **5** was also independently synthesized from *trans*- $[\text{PtH}(\text{CH}_3\text{CN})(\mathbf{1})][\text{BF}_4]$ and methyl acrylate in MeOH -solution, the alcohol presumably acting as a base and deprotonating the $\text{Pt}(\text{II})$ -complex [16]. At *ca.* 0° the ^{31}P -NMR spectrum of **5** shows an *ABX*-pattern for the central resonances (*ABX* for the

Table 2. ^1H -NMR Data for Pt-Complexes of Ligand **1**

Complex	Solvent	$\delta(\text{H} - \text{C}(1), \text{H} - \text{C}(12))$ [ppm]	$\delta(\text{H})^a$ ($^3J(\text{Pt}, \text{H})$) [ppm] ([Hz])
3	CDCl_3	9.77	3.86 (32)
4	CD_2Cl_2	8.15	4.17 (29)
5	CDCl_3	9.68; 10.02	9.20; 3.83; 3.73; 3.36
6	CDCl_3	10.17	3.42; 3.89 (30)
7	CD_2Cl_2^b	9.91	3.47; 4.17 (30)
8	CD_2Cl_2	9.65	3.80 (32)
9	CD_2Cl_2^c	9.50	3.68 (35)
10	CD_2Cl_2^d	10.25	3.85
11	CD_2Cl_2	10.20; 10.77	4.74; 3.90; 3.28; 2.74
13	CD_2Cl_2	10.50	5.55; 4.21 (57)
14	CD_2Cl_2	10.53	5.61; 3.88 (61)
15	C_6D_6	9.30; 9.96	4.08; 4.06; 3.62; 3.58
16	C_6D_6	9.91	3.51; 4.18 (27)

^a) Chemical shift of the 'methylenic' protons; these appear as complex multiplets centered at the value(s) given below (see *P. Boron*, Dissertation 7091 ETH Zürich, 1982, pp. 156–160).

^b) $\delta(\text{CH}_3) = 3.36$. ^c) At -13° . ^d) At -23° .

^{195}Pt -satellites) indicating that rotation of the olefin is restricted. The two significantly different $J(\text{Pt}, \text{P})$ -values (see Table 1) are consistent with the olefinic C-atoms being coplanar or, more likely, nearly coplanar [13] with the P- and Pt-atoms. The ^1H -NMR spectrum of **5** (see also Table 2) could also be assigned on this basis. The multiplets at 1.83 and 2.45 δ were assigned to the alkene geminal protons (*trans* to CO_2Me and to H, respectively) with the third alkene multiplet occurring at 2.74 δ , the CH_3 -resonance being observed at 3.03 δ by analogy with published data for $[\text{Ni}(\text{CH}_2=\text{CH}-\text{CO}_2\text{Me})\{\text{P}(o\text{-OC}_6\text{H}_4\text{CH}_3)_3\}]$ [17].

At room temperature the resonance at 19.9 ppm in the ^{31}P -NMR spectrum of **5** broadened, indicating either an incipient fluxional process or dissociative process.

Alkynes ($\text{RC}\equiv\text{CR}$; $\text{R} = \text{Ph}$, CO_2Me) also displace ethylene from **3**. The products $[\text{Pt}(\text{RC}\equiv\text{CR})(\mathbf{1})]$ ($\text{R} = \text{Ph}$ (**6**); $\text{R} = \text{CO}_2\text{Me}$ (**7**)) were isolated in high yields as yellow, air-stable, mononuclear species. A modification of this procedure, in which a Pt(0)-olefin complex is prepared *in situ* (by addition of **1** to a solution of $[\text{Pt}(\text{COD})_2]$) and then reacted with an alkyne, has enabled isolation of $[\text{Pt}(\text{PhC}\equiv\text{CMe})(\mathbf{1})]$ (**15**). A completely different route to Pt(0)-alkyne complexes of **1** has also been developed in which the Ph_3P -ligands in $[\text{Pt}(\text{RC}\equiv\text{CR}')(\text{PPh}_3)_2]$ are substituted by addition of **1**; in this way the new species $[\text{Pt}(\text{RC}\equiv\text{CR}')(\mathbf{1})]$ ($\text{R} = \text{R}' = \text{CO}_2\text{CH}(\text{CH}_3)_2$, **16**) as well as **6** and **7** have been prepared (see *Experimental*). Complex **7** was also obtained from the reaction of *trans*- $[\text{PtH}(\mathbf{1})(\text{CH}_3\text{CN})][\text{BF}_4]$ with an excess of alkyne and a proton acceptor which can be as weak as MeOH or H_2O . At room temperature there was no evidence for alkyne dissociation from **6**, **7**, **15** and **16** on the NMR time-scale; an observation which is in line with the known behaviour of Ph_3P -complexes $[\text{Pt}(\text{PPh}_3)_2(\text{RC}\equiv\text{CR})]$ [18].

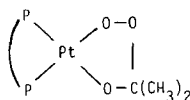
As the complexes $[\text{Pt}(\text{PPh}_3)_n]$ ($n = 3$ or 4) [13] are useful reagents for the preparation of other Pt-species it seemed worthwhile to prepare $[\text{Pt}(\text{PPh}_3)(\mathbf{1})]$ (**8**). Formation of **8** but not of $[\text{Pt}(\text{PPh}_3)_2(\mathbf{1})]$ was found to occur under mild conditions when **3**, freshly prepared *in situ* from $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ and **1**, was treated with an excess of Ph_3P . Unlike

[Pt(PPh₃)₃], **8** undergoes only slow atmospheric degradation in CH₂Cl₂-solution at room temperature. This difference may be related to the slow dissociation of a coordinated phosphine from **8**, behaviour which is atypical for [Pt(PR₃)₃]-species. The ³¹P-NMR spectrum of **8** is of the AB₂-type (AB₂X for the ¹⁹⁵Pt-satellites) and the positions of the observed lines were treated by iterative computer techniques [19] to derive chemical-shift and coupling-constant data (see Table 2). Of these the ²J(P_A,P_B)-value (143 Hz) should be noted since simple zero-valent phosphine complexes [M(PR₃)_n] give rise to [A_n]-³¹P-NMR spectra from which the P,P-coupling is not directly obtainable. It is noteworthy that the signal line widths were *ca.* 2.5 Hz and that even on heating to 70° no significant broadening was observed, though some irreversible decomposition did become apparent. This contrasts with the behaviour of [Pt(PPh₃)₃] which exhibits an exceptionally broad ³¹P-NMR resonance when examined at room temperature.

The Pt(0)-carbonyl complexes [Pt(CO)₂(PPh₃)₂] and [Pt(CO)(PPh₃)₃] [20] have been known for some time but the existence of [Pt(CO)(PPh₃)₂] [21] has been questioned [20]. Thus, it was of interest to establish the nature of the carbonyl complex obtainable in the presence of ligand **1**. When a suspension of [Pt(C₂H₄)(**1**)]_x is treated with CO at room temperature a solution of [Pt(CO)(**1**)] (**9**) is formed virtually quantitatively. This pale yellow solution is somewhat air-sensitive and quickly develops an intense orange-red colour on exposure to the atmosphere. Pale yellow **9** may be obtained either by evaporation of the solvent under a CO-stream or by addition of EtOH to toluene solutions. Under the reaction conditions employed there was no evidence for formation of *pseudo*-tetrahedral [Pt(CO)₂(**1**)]. At room temperature the ³¹P-NMR resonances of **9** were broad but cooling to 250°K allowed collection of accurate chemical shift and J(Pt,P)-values. The ν_{CO} IR-stretching vibration of **9** occurs at 1945 cm⁻¹, in good agreement with that of [Pt(CO)(PPh₃)₂] (1943 cm⁻¹) [21] but it is to be noted one crystalline modification of [Pt(CO)(PPh₃)₃] has a similar value (1942 cm⁻¹) [20]. We have observed that a solution of [Pt(C₂H₄)(PPh₃)₂] treated with CO forms a species with a ³¹P-NMR spectrum (δ = 8.15, J(Pt,P) = 3280 Hz) which is closely comparable to that of **9**; this strongly suggests the formation of [Pt(CO)(PPh₃)₂].

The ¹H- and ³¹P-NMR spectra of solutions obtained by stirring a suspension of **3** in CD₂Cl₂, C₆D₅CH₃ or (D₈)THF, under O₂-atmosphere showed initially the formation of a single new compound. The data (see Tables 1 and 2) were consistent with this complex being [Pt(O₂)(**1**)] (**10**) but, since the solutions quickly decomposed forming unidentified metal complexes and phosphine oxide, an analytically pure sample was not obtained.

When acetone was used as the solvent for this reaction a colourless air-stable complex, which analysed for [Pt{(CH₃)₂CO}(O₂)(**1**)] (**11**) was obtained in high yield. Its ³¹P-NMR spectrum (see Table 1) showed a central AB-pattern indicating that ligand **1** was coordinated in a non-symmetric environment to the metal centre. The ¹H-NMR data (see Table 2) supported this deduction there being *a*) separate signals for the protons H - C(1) and H - C(12) of the phenanthrene ring system, *b*) four multiplets attributable to the methylenic protons of **1** and *c*) two magnetically inequivalent CH₃-groups (δ = 1.35 and 0.93 ppm) for the acetone moiety. As [Pt(O₂)(PPh₃)₂] [22] reacts with acetone to give [(PPh₃)₂PtO₂(CH₃)₂CO] (**12**) [23], it is likely that the oxygen com-

**11**

plex **10** is an intermediate in the formation of **11**. By comparison of the available data we conclude that **11** has a structure analogous to **12** containing a five-membered platinum-cyclic system [23].

The pursuit of various projects involving ligand **1** [24] required the use of complexes of the type *trans*-[PtX(R)(**1**)] and, occasionally, because of the *trans*-configuration of [PtX₂(**1**)]-species [25], conventional procedures [13] failed to yield the desired products. The possibility of using [Pt(C₂H₄)(**1**)]_x (**3**) as a substrate for such syntheses was therefore investigated. As reported in [7], **3** is readily attacked by dry Cl₂-gas to give *cis*-[PtCl₂(**1**)] a molecule with the interesting structural feature of containing ligand **1** showing *cis*-coordination. The Pt-complex **3** reacts smoothly with MeI and PhCH₂Br to generate *trans*-[PtI(Me)(**1**)] (**13**) and *trans*-[PtBr(CH₂Ph)(**1**)] (**14**), respectively. The *trans*-configuration was established by ³¹P- and ¹H-NMR spectra (see *Tables 1* and *2*) [26]. The presence of Pt-C σ-bonded organic ligands was inferred from the presence of ¹H-NMR signals at 0.15 δ (*J*(Pt,H) = 79 Hz) and 2.39 δ (*J*(Pt,H) = 100 Hz) for **13** and **14**, respectively. Thus, complexes of the type **3** are indeed suitable starting materials for the preparation of complexes *trans*-[PtX(R)(**1**)].

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Experimental. – *General.* See [27]. The micro-analytical data for the isolated compounds are given in *Table 3*.

Table 3. Analytical Data for Pt-Complexes of Ligand **1**

Compound	C [%]		H [%]		P [%]		Mol. wt.	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
3	65.27	65.17	4.71	4.52	7.26	7.30	1239	848
4	56.94	55.41	4.65	4.47	5.80	5.50	1359	1127
5	63.92	63.64	4.79	4.45	6.18	6.84	750	906
6 ^{a)}	65.63	65.44	4.21	4.28	5.80	5.72	^{b)}	1083
7	62.48	62.43	4.20	4.19	6.38	6.64	938	962
8	69.28	68.82	4.64	4.56	8.36	8.59	704	1082
9	64.28	63.75	4.12	4.04	6.10	7.31	1100	848
11	62.07	62.04	4.55	4.43	6.73	6.81	941	910
13 ^{c)}	55.97	56.20	3.85	3.88	6.57	6.44	^{d)}	962
14 ^{e)}	60.46	60.50	4.51	4.12	5.65	6.08	^{b)}	991
15	68.03	68.02	4.70	4.52	^{b)}	6.63	^{b)}	936
16	64.82	63.72	5.41	4.76	^{b)}	6.10	^{b)}	1018

^{a)}CH₂Cl₂. ^{b)}Not determined. ^{c)}I [%]: Found 12.91; Calc. 13.20. ^{d)}Too insoluble for this determination.

^{e)}1/3 CH₂Cl₂.

$[Pt(C_2H_4)(1)]_x$ ($x = 1$ or 2) (3). A suspension of $[Pt(COD)_2]$ (410 mg, 1 mmol) in toluene (10 ml) at 0° was stirred under an ethylene atmosphere to produce $[Pt(C_2H_4)_3]$ *in situ*. To this stirred clear yellow solution was added portionwise solid ligand **1** (625 mg, 1 mmol); evolution of gas was observed and a white precipitate formed. After $\frac{1}{2}$ h at r.t. the solid was filtered off (0° , N_2 -atmosphere) and the eluate set aside (solution A). The solid was washed successively with acetone (5 ml), CH_2Cl_2 (2 ml) and Et_2O (10 ml) and then dried *in vacuo*: yield 650 mg (77%). So prepared, the complex was found to be analytically pure; attempted recrystallizations of this material were unsuccessful owing to its low solubility.

$[(C_2H_4)_2Pt(1)Pt(C_2H_4)_2]$ (4). If the solution A (see *above*) was saturated with ethylene at 0° and then cooled (-20° , 4 days) small amounts of dark orange crystalline **4** were obtained: yield 50–100 mg (4–9%) (Addition of light petroleum ether to the solution to improve the yield generally resulted in the formation of a precipitate which contained a mixture of products).

$[Pt(CH_2=CHCO_2Me)(1)]$ (5). To a suspension of **3** (200 mg, 0.236 mmol) in acetone (5 ml) was added excess methyl acrylate (5 ml) and the solution refluxed for 10 min. Solvent and olefin were then allowed to boil off under a stream of N_2 and the resulting pale yellow solid extracted with CH_2Cl_2 (10 ml) and filtered (*ca.* 10 mg of insoluble material). The solution was concentrated to *ca.* 2 ml and the pale yellow complex precipitated with Et_2O , collected and dried *in vacuo*. M.p. $> 150^\circ$ (dec.); yield 180 mg (84%).

$[Pt(PhC\equiv CPh)(1)]$ (6). To a suspension of **3** (423 mg, 0.5 mmol) in toluene (5 ml) was added excess diphenylacetylene (1 g) and the solution warmed to 60° . During 15 min the suspended solid became pale yellow and after evaporating to dryness *in vacuo* and washing with Et_2O the product was recrystallized from CH_2Cl_2/Et_2O to give **6** as its CH_2Cl_2 solvate: yield 450 mg (88%).

$[Pt(MeO_2CC\equiv CCO_2Me)(1)]$ (7). This complex was prepared as described for **6** from **3** (423 mg, 0.5 mmol) and $C_2(CO_2Me)_2$ (1 g, excess). It is pale yellow crystalline material of m.p. $> 230^\circ$ (dec.); yield 375 mg (78%).

$[Pt(PPh_3)(1)]$ (8). $[Pt(COD)_2]$ (205 mg, 0.5 mmol) was added to toluene (5 ml), which had been saturated with ethylene, at r.t. The addition of ligand **1** (310 mg, 0.5 mmol) to the clear yellow solution obtained above gave a solution of similar colour (with C_2H_4 -evolution) and solid Ph_3P (261 mg, 1 mmol) was added before **3** began to precipitate. Further C_2H_4 was evolved and a clear orange solution was obtained. Changing to a N_2 -atmosphere, addition of light petrol (20 ml) precipitated the orange compound which was collected, washed with further petrol ether (15 ml) and dried *in vacuo*. The crude product was recrystallized from toluene/light petrol. M.p. 250 – 252° , yield 405 mg (75%).

$[Pt(CO)(1)]$ (9). A slow O_2 -free stream of CO was bubbled into a stirred suspension of **3** (212 mg, 0.25 mmol) in CH_2Cl_2 (5 ml) under N_2 and after a few minutes a very pale yellow clear solution was obtained. After concentrating the solution to *ca.* 2 ml using a CO-stream, the complex was precipitated by addition of $EtOH$ (10 ml). The pale yellow solid was collected, washed with Et_2O (5 ml) and dried *in vacuo*. M.p. $> 150^\circ$ (dec.); yield 190 mg (90%). Recrystallization from CH_2Cl_2/Et_2O was possible under a CO-atmosphere but if extreme care was not taken to prevent contamination with O_2 the product became discoloured with dark orange-red impurities.

$[Pt(O_2)(1)]$ (10). A solution of this compound was prepared as follows: **3** was suspended in the appropriate deuterated solvent under an O_2 -atmosphere. The vessel was sealed and warmed to 35° with stirring. After the solution had acquired a dark orange colour (5 to 15 min depending on the solvent) the mixture was filtered into a 1H -NMR tube and spectra run shortly afterwards. For ^{31}P -NMR spectra non-deuterated solvents (2 ml) were used with an (D_6)acetone capillary as 'lock'.

$[(1)PtO_2(CH_3)_2CO]$ (11). A suspension of (200 mg, 0.236 mmol) in acetone (15 ml) was stirred under an O_2 -atmosphere for 16 h. Evaporation of the solution *in vacuo* gave an off-white solid which was extracted with CH_2Cl_2 (20 ml). On slow concentration the solution deposited white needles of m.p. $> 120^\circ$ (dec.); yield 155 mg (72%). **11** can be recrystallized from acetone.

$[Pt(Me)(1)]$ (13). A suspension of **3** (400 mg, 0.472 mmol) in toluene (10 ml) was treated with excess MeI (3 ml) and warmed to 50° for 15 min. The solid and solution acquired a slight yellow-colour and an off white solid was obtained on evaporation of solvent and excess MeI *in vacuo*. The sparingly soluble product was extracted with CH_2Cl_2 (*ca.* 30 ml), the solution concentrated to *ca.* 5 ml and Et_2O (10 ml) added. The white product was filtered off, washed with Et_2O and dried *in vacuo*. M.p. $> 300^\circ$; yield 405 mg (89%).

[*PtBr(CH₂Ph*) (**1**)] (**14**). This compound may be prepared as described above for **13** using **3** and PhCH₂Br. The complex is somewhat more soluble than **13** and was obtained in 86% yield as a pale yellow solid; m.p. > 300°.

[*Pt(Ph≡CMe*) (**1**)] (**15**). A stirred solution of [Pt(COD)₂] (150 mg, 0.365 mmol) in *ca.* 2 ml THF was cooled to 0° and **1** (228 mg, 0.365 mmol) added dropwise as a solution in THF (2 ml). At this temp. excess 3-phenyl-2-propyne (135 μl, 1.093 mmol) was added with a microsyringe and the mixture allowed to come to r.t. After stirring for 1 h the yellow solution was concentrated *in vacuo* to *ca.* 2 ml. Cooling to –20° produced crystals of **15** which were filtered off, washed with Et₂O and dried *in vacuo*. M.p. > 201°; yield 269 mg (79%).

[*Pt(RC≡CR')*] (**1**) (*R = R' = CO₂CH(CH₃)₂*) (**16**). This was prepared according to the following general method that is also applicable for **7** (*R = R' = CO₂Me*). To a solution of [Pt(RC≡CR')(PPh₃)₂] (0.100 mmol) in a few ml of CH₂Cl₂ was added a small excess of solid **1** (0.105 mmol) to produce a clear yellow solution which was stirred for 0.5 h at r.t. Addition of Et₂O produced a precipitate which was filtered off and recrystallized from CH₂Cl₂/Et₂O to give the pure yellow product (**16** or **7**) in *ca.* 90% yield. M.p. > 215°. Complex **6** (*R = R' = Ph*) can also be synthesized using the above method (86% yield) but in this case a 10-fold excess of free PhC≡CPh must be present during the phosphine-substitution reaction.

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