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REACTIONS OF DIPHOSPHINEPLATINUM(II) OXALATE COMPLEXES WITH PHENYLACETYLENE. FORMATION OF PHENYLALKYNYLPLATINUM COMPLEXES

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Summary

$[Pt(C_2O_4)(dppe)]$ reacts thermally with $PhC{\equiv}CH$ to produce $[Pt(C{\equiv}CPh)_2(dppe)]$, which has been prepared by alternative routes. Similar treatment of $[Pt(C_2O_4)(dppm)]$ initially produces $[Pt(C{\equiv}CPh)_2(dppm)]$, which rearranges to give *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$. Reaction of $[PtCl_2(dppm)]$ with $PhC{\equiv}CH$/KOH/18-crown-6, or with $(PhC{\equiv}C)SnMe_3$, gives $[Pt(C{\equiv}CPh)_2(dppm)]$, which may be converted to the *cis,cis*-dimer by addition of oxalic acid. Ultraviolet irradiation or refluxing with a trace amount of dppm converts $[Pt(C{\equiv}CPh)_2(dppm)]$ to *trans,trans*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$, but the *cis,cis*-dimer is stable under these conditions. $[Pt(C_2O_4)L_2]$ ($L = PPh_3$, PEt_3) complexes also react thermally with $PhC{\equiv}CH$ to yield $[Pt(C{\equiv}CPh)_2L_2]$ species.

Introduction

Photochemical generation of PtL_2 (L = tertiary phosphine) fragments from the corresponding oxalate complexes, with concomitant elimination of 2 mol. equiv. of CO_2, has been known for a number of years [1–3], and this approach has recently been used to advantage by Trogler in preparing a variety of complexes via the photochemically produced $Pt(PEt_3)_2$ moiety and the reactive $[Pt(PEt_3)_2(C_2H_4)]$ complex [4,5]. We have been investigating the photochemistry of platinum(II) oxalate complexes containing diphosphine ligands in which the PtL_2 fragments generated will have two phosphino groups constrained in mutually *cis* positions. The results of this photochemical study will be presented elsewhere, but we report here the reactions of some platinum(II) oxalate complexes with phenylacetylene.

Blake and Nyman have reported the formation of *trans*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ when $[Pt(C_2O_4)(PPh_3)_2]$ is irradiated in the presence of phenylacetylene [2]. Furthermore, they suggested that the bis(phenylalkynyl) complex is formed by two successive oxidative additions of $PhC{\equiv}CH$ to $Pt(PPh_3)_2$ followed by reductive elimination

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of hydrogen. We have now found that the reactions of $[Pt(C_2O_4)L_2]$ (L = tertiary phosphine or L_2 = diphosphine) complexes with phenylacetylene are not photochemical in nature. Rather, these complexes react thermally with phenylacetylene to produce the bis(phenylalkynyl) complexes and oxalic acid.

Results and discussion

The platinum(II) oxalate complexes were prepared by the reaction of $[PtCl_2L_2]$ (L = PEt_3, PPh_3 or L_2 = dppe, dppm) with silver(I) oxalate in a manner similar to that described by Trogler [5]. Their infrared and $^{31}P\{^1H\}$ NMR parameters are given in Tab. 1.

When an acetonitrile or dichloromethane solution of $[Pt(C_2O_4)(dppe)]$ is treated with excess phenylacetylene the color of the solution changes from light yellow to reddish-brown within a few hours. After standing at ambient temperature for two days the $^{31}P\{^1H\}$ NMR spectrum of such a solution indicates that complete conversion to $[Pt(C{\equiv}CPh)_2(dppe)]$ has occurred, the resonance at $\delta(P)$ 32.7, $^1J(Pt,P)$ 3628 Hz due to $[Pt(C_2O_4)(dppe)]$ having been replaced by a new signal at $\delta(P)$ 41.2, $^1J(Pt,P)$ 2261 Hz. The identity of the bis(phenylalkynyl)platinum complex was confirmed by comparison with a sample prepared by the method of Pidcock [6] ($\delta(P)$ 41.1, $^1J(Pt,P)$ 2280 Hz in $CDCl_3$, $\nu(C{\equiv}C)$ 2112 cm^{-1} (KBr pellet)).

As an alternative route to alkynylplatinum complexes we have investigated the reaction of $[PtCl_2(dppe)]$ with $(PhC{\equiv}C)SnMe_3$ [7,8]. Initially we attempted to prepare $[PtCl(C{\equiv}CPh)(dppe)]$. Treatment of a CH_2Cl_2 solution of $[PtCl_2(dppe)]$ with 1 mol. equiv. of $(PhC{\equiv}C)SnMe_3$ at ambient temperature results in a 1/1 mixture of $[PtCl_2(dppe)]$ and $[Pt(C{\equiv}CPh)_2(dppe)]$. This contrasts with the work of Lappert [8] on complexes containing monodentate phosphines where he was able to isolate complexes of the type *trans*-$[PtCl(C{\equiv}CPh)L_2]$. In the case of the dppe complexes it is clear that the rate of eq. 2 exceeds that of eq. 1. The increased rate of substitution of the second chloride may be due to a *cis*-effect from the phenylalkynyl ligand, or it may be indirectly produced by the modified *trans*-effect of dppe after introduction of the first phenylalkynyl group.

$$[PtCl_2(dppe)] + (PhC{\equiv}C)SnMe_3 \rightarrow [PtCl(C{\equiv}CPh)(dppe)] + Me_3SnCl \qquad (1)$$

$$[PtCl(C{\equiv}CPh)(dppe)] + (PhC{\equiv}C)SnMe_3 \rightarrow [Pt(C{\equiv}CPh)_2(dppe)] + Me_3SnCl \qquad (2)$$

TABLE 1

INFRARED AND $^{31}P\{^1H\}$ NMR DATA FOR THE PLATINUM(II) OXALATE COMPLEXES

Complex	$\nu(C{=}O)$ (cm^{-1})	$\nu(C-O)+\nu(C-C)$ (cm^{-1})	$\delta(P)$ [a]	$^1J(Pt,P)$ (Hz)
$[Pt(C_2O_4)(dppe)]$	1705vs, 1678vs	1356vs	32.7	3628
$[Pt(C_2O_4)(dppm)]$	1699vs, 1678vs, 1666s	1357vs	−63.7	3081
$[Pt(C_2O_4)(PEt_3)_2]$	1696vs, 1680vs, 1665s	1360vs	5.0	3523
$[Pt(C_2O_4)(PPh_3)_2]$	1712vs, 1705sh, 1678s	1345vs	7.6	3777

[a] Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding.

When $[PtCl_2(dppm)]$ is treated with phenylacetylene in the presence of KOH and 18-crown-6 the novel complex $[Pt(C{\equiv}CPh)_2(dppm)]$ is obtained in good yield. The product was characterized by elemental analysis, as well as its infrared and $^{31}P\{^1H\}$ NMR spectra. The infrared spectrum exhibits a peak at 2108 cm^{-1} due to $\nu(C{\equiv}C)$, and the $^{31}P\{^1H\}$ NMR spectrum contains a high field resonance at $\delta(P)$ -55.8, typical of chelated dppm [9], with a $^1J(Pt,P)$ coupling constant of 1916 Hz. The bis(phenylalkynyl)platinum complex may also be prepared by treatment of $[PtCl_2(dppm)]$ with $(PhC{\equiv}C)SnMe_3$, but only when a large excess of the tin reagent is employed; even then the reaction is incomplete after two days at ambient temperature. As in the case when dppe is used the reaction proceeds to give the bis(phenylalkynyl) complex, indicating that substitution of the second chloride is again easier than the first. The lower overall reaction rate for $[PtCl_2(dppm)]$ compared to its dppe analogue is likely to be due to the lower *trans*-effect of the diphenylphosphino moiety when it is held in a 4-membered chelate ring.

While this work was in progress a report appeared [10] of the preparation of a series of methylalkynyl complexes of platinum containing $R_2PCH_2PR_2$ ligands ($R = Ph$, Me, Et, i-Pr). With dppm the complexes $[Pt(C{\equiv}CMe)_2(dppm)]$ and *trans,trans*-$[Pt_2(C{\equiv}CMe)_4(\mu\text{-dppm})_2]$ were obtained, and complexes of the type *trans,trans*-$[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ had been reported previously by Shaw [11]. In the case of bis(diethylphosphino)methane (depm) four complexes were characterized spectroscopically, namely $[Pt(C{\equiv}CMe)_2(depm)]$ and *cis,cis*-, *cis,trans*- and *trans,trans*-$[Pt_2(C{\equiv}CMe)_4(\mu\text{-depm})_2]$ [10].

When a CH_3CN solution of $[Pt(C_2O_4)(dppm)]$ is treated with excess phenylacetylene the solution darkens and, within a few hours, $[Pt(C{\equiv}CPh)_2(dppm)]$ is formed. However, before this reaction is complete a subsequent rearrangement occurs to yield a dimeric species which we assign as *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$, by comparison of its $^{31}P\{^1H\}$ NMR spectrum (Tab. 2) with those reported by Puddephatt for analogous *cis,cis*-dimers [10,12]. After one week at ambient temperature the conversion to *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$ is complete. The monomeric complex, prepared from $[PtCl_2(dppm)]$ and $PhC{\equiv}CH/KOH$, is stable in CH_2Cl_2 or CH_3CN solution for several days at ambient temperature, and refluxing in benzene solution for 16 h causes virtually no change in the $^{31}P\{^1H\}$ NMR spectrum of the solution. Stirring with excess phenylacetylene in CH_3CN solution for one week also causes no reaction. However, the addition of oxalic acid causes the rearrangement to *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$. Treatment of a CH_3CN/C_6H_6 (3/1) solution of $[Pt(C{\equiv}CPh)_2(dppm)]$ with excess $H_2C_2O_4 \cdot 2H_2O$ produces $[Pt(C_2O_4)(dppm)]$ and a small amount of the *cis,cis*-dimer, whereas addition of a stoichiometric amount of $H_2C_2O_4 \cdot 2H_2O$ gives *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$ and $[Pt(C_2O_4)(dppm)]$ in an approximately 3/1 ratio (as estimated from the $^{31}P\{^1H\}$ NMR spectrum), after 5 d at ambient temperature. Thus it is the oxalic acid produced in the reaction of $[Pt(C_2O_4)(dppm)]$ with phenylacetylene which catalyzes the dimerization of $[Pt(C{\equiv}CPh)_2(dppm)]$ to yield *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$. Treatment of the *cis,cis*-dimer with excess oxalic acid does not regenerate $[Pt(C_2O_4)(dppm)]$ indicating that whereas $[Pt(C_2O_4)(dppm)]$ and $[Pt(C{\equiv}CPh)_2(dppm)]$ exist in equilibrium in the presence of $PhC{\equiv}CH$ and oxalic acid, the *cis,cis*-dimer is formed irreversibly and represents the thermodynamically most stable complex of the three.

Whereas $[Pt(C{\equiv}CPh)_2(dppm)]$ is stable in refluxing benzene, addition of a trace of free dppm to such a solution results in quantitative conversion to *trans,trans*-

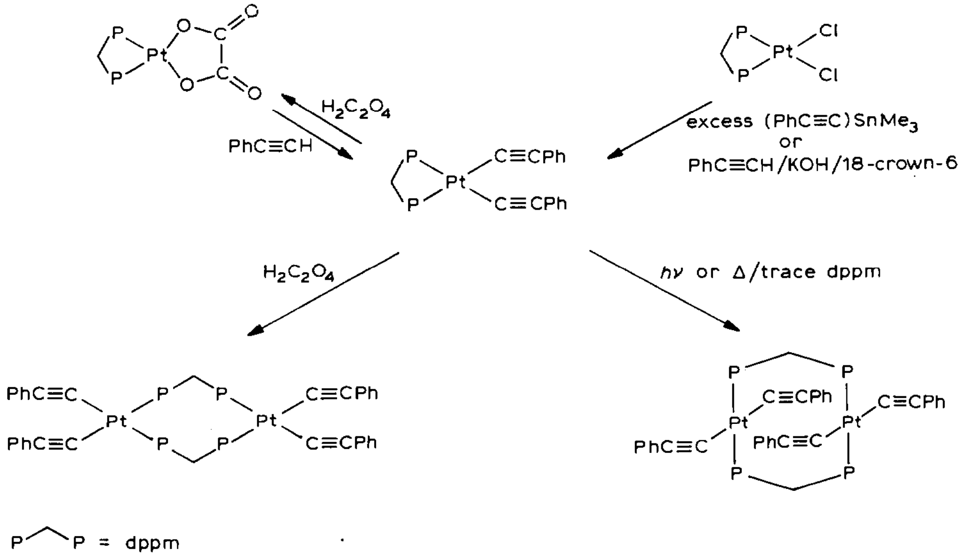
TABLE 2

$^{31}P\{^1H\}$ NMR DATA FOR THE PHENYLALKYNYLPLATINUM(II) COMPLEXES

Complex	$\delta(P)$ [a]	$^1J(Pt,P)$ (Hz)	other couplings
$[Pt(C\equiv CPh)_2(dppe)]$	41.1	2280	
$[Pt(C\equiv CPh)_2(dppm)]$	-55.8	1916	
cis,cis-$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$ [b]	-1.8	2396	$^3J(Pt,P)$ 55 Hz [c] $^2J(P,P)+{}^4J(P,P)$ 23 Hz
trans,trans-$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$ [d]	1.1	2777	$^3J(Pt,P)$ 50 Hz [c] $^2J(P,P)+{}^4J(P,P)$ 28 Hz
trans-$[Pt(C\equiv CPh)_2(PPh_3)_2]$	17.3	2988	
cis-$[Pt(C\equiv CPh)_2(PEt_3)_2]$	4.4	2244	

[a] Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. [b] Recorded in CH_2Cl_2 solution. [c] Obtained by a peak assignment similar to that of Puddephatt (ref. 10). [d] Recorded in CH_3CN/C_6H_6 (3/1) solution.

$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$ (Tab. 2) after refluxing for 4 h. A similar rearrangement has been reported for $[Pt(C\equiv CMe)_2(dppm)]$, although the reaction was incomplete after one month at ambient temperature [10]. Ultraviolet irradiation of a CH_3CN/C_6H_6 (3/1) solution of $[Pt(C\equiv CPh)_2(dppm)]$ for 16 h also results in quantitative formation of *trans,trans*-$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$. A similar irradiation of *cis,cis*-$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$, on the other hand, causes virtually no change in the $^{31}P\{^1H\}$ NMR spectrum of the solution. Likewise, refluxing a CH_3CN/C_6H_6 (3/1) solution of *cis,cis*-$[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$ with a trace of free dppm for 30 min causes no change in the $^{31}P\{^1H\}$ NMR spectrum. The methods of formation and reactions of the bis(phenylalkynyl)platinum complexes containing dppm are summarized in Scheme 1.



SCHEME 1. Formation and reactions of bis(phenylalkynyl)platinum complexes containing dppm.

It has been suggested [10] that for bis(methylalkynyl)platinum complexes containing $R_2PCH_2PR_2$ the species formed are strongly dependent on the bulk of R. For R = i-Pr only the monomer was observed, whereas addition of a trace of PPh_3 to a solution of [Pt(C≡CMe)$_2$(depm)] (R = Et) caused rearrangement initially to a mixture of *cis,cis*- and *cis,trans*-[Pt$_2$(C≡CMe)$_4$(μ-depm)$_2$], followed by the appearance of the *trans,trans*-dimer. This pointed to an initial stereospecific substitution at platinum, followed by a slower isomerization step [10]. With dppm only the monomer and *trans,trans*-dimer were detected, the latter being the more thermodynamically stable. In this work we find *cis,cis*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] to be remarkably stable, once formed, but it is only formed from [Pt(C≡CPh)$_2$(dppm)] under mild conditions. The fact that the *cis,cis*-dimer is stable to irradiation or refluxing with free dppm, these being the conditions under which [Pt(C≡CPh)$_2$(dppm)] is converted to the *trans,trans*-dimer, precludes the involvement of *cis,cis*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] as an intermediate in this process.

Platinum(II) oxalate complexes containing monodentate phosphine ligands also react thermally with phenylacetylene to yield bis(phenylalkynyl)platinum compounds. When a CH_3CN solution of [Pt(C_2O_4)(PPh_3)$_2$] is treated with excess phenylacetylene the solution darkens and the $^{31}P\{^1H\}$ NMR spectrum indicates quantitative formation of *trans*-[Pt(C≡CPh)$_2$(PPh_3)$_2$] (δ(P) 17.3, ^1J(Pt,P) 2988 Hz). This result shows that the presumption of Blake and Nyman [2], that this reaction is photochemical, is incorrect. Similarly, addition of excess PhC≡CH to a CH_3CN solution of [Pt(C_2O_4)(PEt_3)$_2$] results in quantitative formation of a new species (δ(P) 4.4, ^1J(Pt,P) 2244 Hz) which we believe is *cis*-[Pt(C≡CPh)$_2$(PEt_3)$_2$]. Attempts to convert this to the *trans*-isomer [6,13,14] by heating with a trace of free PEt_3 resulted only in extensive phosphine dissociation.

Experimental

1,2-Bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm), phenylacetylene, trimethyltin chloride, oxalic acid and 18-crown-6 were obtained from commercial suppliers and used without further purification. [PtCl$_2$(dppe)] [15], [PtCl$_2$(dppm)] [15], and $Ag_2C_2O_4$ [5] were prepared according to established procedures. Infrared spectra were recorded for KBr pellets on a Perkin–Elmer 783 spectrophotometer. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$ unless otherwise stated) were recorded on a JEOL FX-100 NMR spectrometer operating in the FT mode. ^1H NMR spectra were obtained using a Varian T-60 instrument. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Preparation of [Pt(C_2O_4)(dppe)]

To a CH_2Cl_2 solution of [PtCl$_2$(dppe)] (1.88 g, 2.83 mmol) was added a slight excess of silver oxalate (1.07 g, 3.51 mmol). The mixture was stirred for several days in the absence of light, then filtered to remove AgCl and unreacted $Ag_2C_2O_4$. The filtrate was evaporated to 10 ml, and ether was added which precipitated an off-white solid. This was filtered, washed with ether, and dried by suction to give [Pt(C_2O_4)(dppe)] (1.84 g, 95%). Found: C, 49.05; H, 3.71. $C_{28}H_{24}O_4P_2Pt$ calcd.: C, 49.35; H, 3.55%. [Pt(C_2O_4)(dppm)] was prepared similarly. Found: C, 48.49; H, 3.43. $C_{27}H_{22}O_4P_2Pt$ calcd.: C, 48.58; H, 3.32%. [Pt(C_2O_4)(PEt_3)$_2$] and [Pt(C_2O_4)-

$(PPh_3)_2]$ were prepared similarly and identified by their $^{31}P\{^1H\}$ NMR and infrared spectra [5].

Preparation of [Pt(C≡CPh)₂(dppe)]

This compound was prepared by a slight modification of the method of Almeida and Pidcock [6]. $[PtCl_2(dppe)]$ (0.57 g, 0.86 mmol) was suspended in phenylacetylene (7 ml). An aqueous solution of KOH (0.22 g, 3.95 mmol) and 18-crown-6 (0.12 g, 0.45 mmol) was added, and the mixture was stirred under nitrogen at 50°C for two hours. The solvents were removed, the residue was dissolved in CH_2Cl_2 and poured into a separating funnel containing water. After shaking vigorously, the layers were allowed to separate, and the organic layer was collected. The aqueous layer was extracted with several portions of CH_2Cl_2, and the organic layers were combined, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to 5 ml, and addition of ether gave the product as a yellow solid (0.43 g, 64%), which was identified as $[Pt(C{\equiv}CPh)_2(dppe)]$ by comparison of its $^{31}P\{^1H\}$ NMR and infrared spectra with those previously reported [6].

Preparation of [Pt(C≡CPh)₂(dppm)]

This compound was prepared as above, but was precipitated from CH_2Cl_2 solution by addition of ethanol. The product was filtered, washed with ethanol and ether, and suction dried. Found: C, 62.68; H, 4.20. $C_{41}H_{32}P_2Pt$ calcd.: C, 62.99; H, 4.13%.

Preparation of trimethyl(phenylethynyl)stannane

To 50 ml of dry ether was added 50 ml of a 1.5 *M* solution of n-butyllithium in hexane under argon. A solution of phenylacetylene (8 ml) in dry ether (50 ml) was added dropwise with stirring at 0°C. This resulted in a brown solution, which was stirred for an additional hour. A solution of Me_3SnCl (14.5 g, 72.8 mmol) in ether was added dropwise whilst cooling to 0°C, and a white precipitate (presumably LiCl) and a yellow solution were formed. After allowing to warm to room temperature and stirring overnight, the mixture was hydrolyzed, at 0°C, with a saturated ammonium chloride solution, then transferred to a separating funnel containing 50 ml of water. The mixture was shaken vigorously, the layers were allowed to separate, and the yellow ether layer was collected and dried over anhydrous magnesium sulfate. After filtration the ether was removed and the residue was distilled at 77–79°C (0.5 torr) to give $(PhC{\equiv}C)SnMe_3$ as a colorless liquid in 70% yield. On cooling to −10°C the product solidified to give white, needle-like crystals. IR (neat): $\nu(C{\equiv}C)$ 2137s cm^{-1}; $\delta(C{-}H)$ 755s cm^{-1}; 690s cm^{-1} (monosubstituted aromatic ring). ^1H NMR ($CDCl_3$) δCH_3 0.3, $^2J(Sn,H)$ 59 Hz (relative intensity 9), $\delta(C_6H_5)$ 7.1–7.7 (5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta(C(CH_3))$ −7.9, $^1J(^{119}Sn{-}C)$ 403 Hz, $^1J(^{117}Sn{-}C)$ 385 Hz, $\delta(C(C{\equiv}C))$ 93.6 and 108.8 ($J(Sn,C)$ not observed), $\delta(C(C_6H_5))$ 123.4, 127.9 and 131.6 ppm.

Reaction of [PtCl₂(dppe)] with (PhC≡C)SnMe₃

Equimolar amounts of $[PtCl_2(dppe)]$ and $(PhC{\equiv}C)SnMe_3$ were mixed in CH_2Cl_2 solution. On standing overnight the solution turned yellow, and its $^{31}P\{^1H\}$ NMR spectrum indicated the presence of $[PtCl_2(dppe)]$ and $[Pt(C{\equiv}CPh)_2(dppe)]$ in a 1/1 ratio.

Reaction of [PtCl$_2$(dppm)] with (PhC≡C)SnMe$_3$

When [PtCl$_2$(dppm)] and 2 mol equiv. (PhC≡C)SnMe$_3$ were allowed to stand overnight in CH_2Cl_2 solution the $^{31}P\{^1H\}$ NMR spectrum indicated that no reaction had occurred. A large excess of (PhC≡C)SnMe$_3$ was added and the solution was allowed to stand for a further two days. The $^{31}P\{^1H\}$ NMR spectrum then showed that [Pt(C≡CPh)$_2$(dppm)] and [PtCl$_2$(dppm)] were present in a 2/1 ratio.

Reaction of [Pt(C_2O_4)L_2] (L_2 = dppe, dppm; L = PEt$_3$, PPh$_3$) with phenylacetylene

The oxalate complex was dissolved in CH_3CN or CH_2Cl_2 and excess phenylacetylene was added. The pale yellow solution darkened to reddish-brown and after 2 d the $^{31}P\{^1H\}$ NMR spectrum indicated that complete conversion to the bis(phenylalkynyl)platinum complex had occurred. In the case of [Pt(C_2O_4)(dppm)] the initial product was [Pt(C≡CPh)$_2$(dppm)], but on standing for several days this was quantitatively converted to *cis,cis*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$].

Reaction of [Pt(C≡CPh)$_2$(dppm)] with dppm

To a benzene solution of [Pt(C≡CPh)$_2$(dppm)] (33 mg) was added a trace amount of dppm, and the solution was refluxed for 4 h. The solvent was removed and the residue was dissolved in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of this solution indicated that quantitative conversion to *trans,trans*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] had occurred.

Irradiation of [Pt(C≡CPh)$_2$(dppm)]

A solution of [Pt(C≡CPh)$_2$(dppm)] in CH_3CN/C_6H_6 (3/1) was placed in a quartz tube and irradiated for 16 h with 254 nm radiation using a Rayonet RS photochemical reactor. The $^{31}P\{^1H\}$ NMR spectrum indicated that complete conversion to *trans,trans*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] had taken place.

Reaction of [Pt(C≡CPh)$_2$(dppm)] with oxalic acid

(a) Excess oxalic acid dihydrate was introduced into a CH_3CN/C_6H_6 (3/1) solution of [Pt(C≡CPh)$_2$(dppm)]. After standing overnight the $^{31}P\{^1H\}$ NMR spectrum showed the presence of [Pt(C_2O_4)(dppm)] and a small amount of *cis,cis*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$]. (b) Treatment of a CH_3CN/C_6H_6 (3/1) solution of [Pt(C≡CPh)$_2$(dppm)] with 1 mol equiv. $H_2C_2O_4 \cdot 2H_2O$ produced, after standing overnight, [Pt(C_2O_4)(dppm)] and *cis,cis*-[Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] in a 1/3 ratio.

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