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REACTIONS OF ZERO-VALENT PLATINUM COMPLEXES WITH SOME DIACETYLENES *

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Summary

The complexes $[Pt(C_2H_4)L_2]$ (L = PPh_3 or $PMePh_2$) react with 1,4-diphenylbuta-1,3-diyne to give, successively, mono- and di-platinum compounds $[Pt(PhC_4Ph)L_2]$ and $[Pt_2(PhC_4Ph)L_4]$. Hexa-2,4-diyne and $[Pt(C_2H_4)(PPh_3)_2]$ react similarly. In the di-platinum compounds both acetylenic linkages are η^2-bonded to platinum atoms, as also occurs in the complex $[Pt_2\{HC_2(CH_2)_2C_2H\}(PPh_3)_4]$ obtained from hexa-1,5-diyne. Reaction of $[Pt_3(CN\text{-t-Bu})_6]$ with 1,4-diphenylbuta-1,3-diyne and hexa-2,4-diyne affords di-platinum complexes, shown by spectroscopic studies to have structures containing diplatinacyclobutene rings.

Introduction

Bis(cycloocta-1,5-diene)platinum [1] has been shown to be a useful precursor in the synthesis of many types of organoplatinum compounds [2]. One aspect of our work has involved the preparation and structural characterisation of new acetylene complexes, and as part of this study [3—6] we have so far identified compounds corresponding to the structural types A—G (Fig. 1). Our research hitherto has been limited to mono-acetylenes. In this paper we describe some studies involving di-acetylenes. Previously, one such complex of platinum has been described, namely, $[Pt(\eta^2\text{-MeC}\equiv\text{CC}\equiv\text{CMe})(PPh_3)_2]$, being obtained by reduction of $[PtCl_2(PPh_3)_2]$ with hydrazine in the presence of hexa-2,4-diyne [7].

Results and discussion

Reactions of $[Pt(C_2H_4)L_2]$ (L = PPh_3 or $PMePh_2$) with the acetylenes $RC\equiv CC\equiv CR$ (R = Me or Ph) and $HC\equiv CCH_2CH_2C\equiv CH$ were investigated. The

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

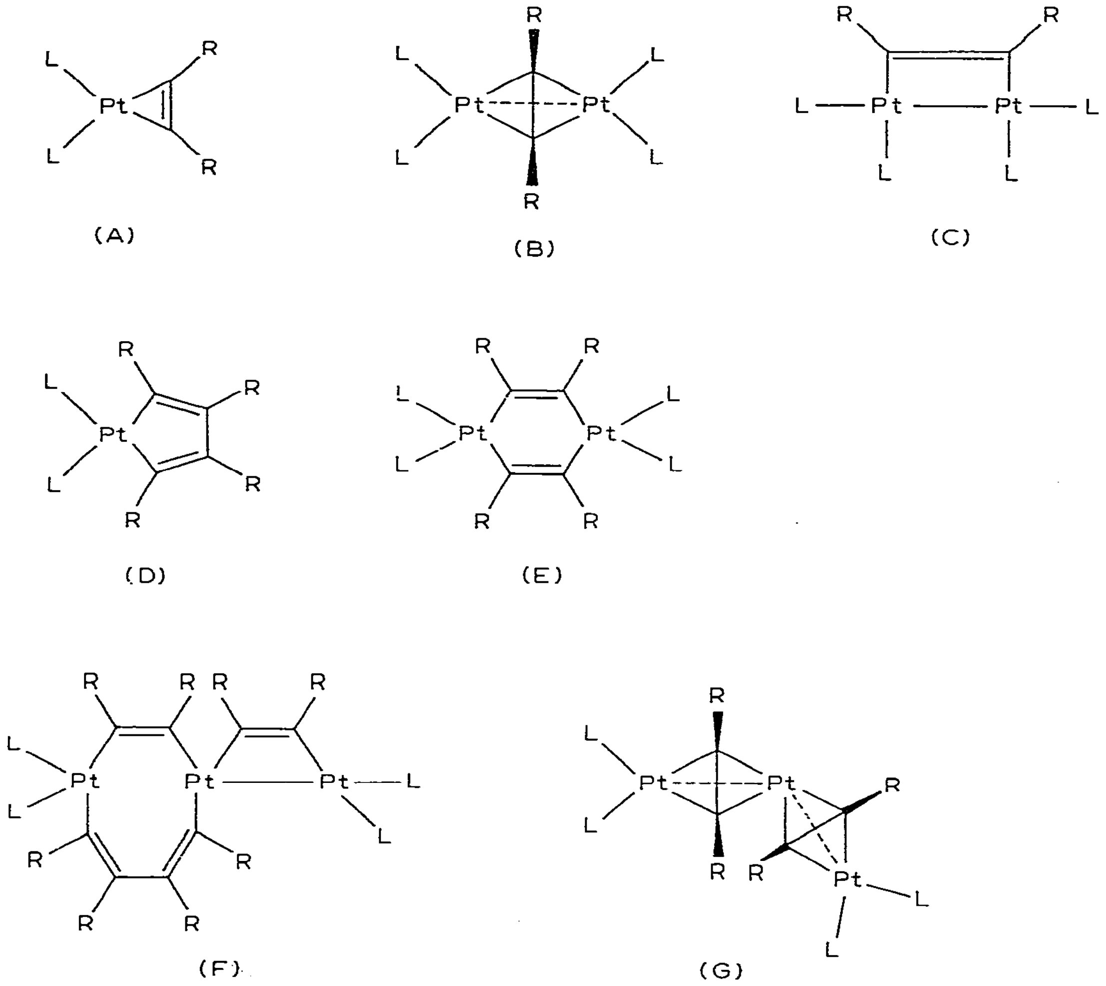


Fig. 1. The ligands L can be R_3P or RNC, or L_2 can be RC≡CR or 1,5-C_8H_{12}, depending on the syntheses involved; see ref. 3, 5 and 6.

complexes ethylenebis(tertiaryphosphine)platinum were conveniently prepared from $[Pt(1,5\text{-}C_8H_{12})_2]$ by adding the latter to ethylene-saturated light petroleum at 0°C, so as to generate $[Pt(C_2H_4)_3]$ in situ. A stoichiometric amount of triphenyl- or diphenylmethyl-phosphine was then added, affording the species $[Pt(C_2H_4)L_2$ quantitatively.

Treatment of $[Pt(C_2H_4)(PPh_3)_2]$, suspended in light petroleum at room temperature, with an equimolar amount of 1,4-diphenylbuta-1,3-diyne afforded the complex I in high yield. The infrared spectrum of this complex (Table 1) showed the presence of un-coordinated (2170 cm^{-1}) and coordinated (1725 cm^{-1}) C≡C stretching frequencies, in accord with the attachment of one platinum atom to the acetylene as in A (Fig. 1). Reaction of complex I with a second equivalent of $[Pt(C_2H_4)(PPh_3)_2]$ gives compound II. As expected, the infrared spectrum of the latter shows no band near 2140 cm^{-1} corresponding to

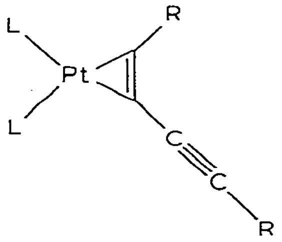
TABLE 1

INFRARED AND ^{31}P NMR DATA FOR THE DI-ACETYLENE COMPLEXES

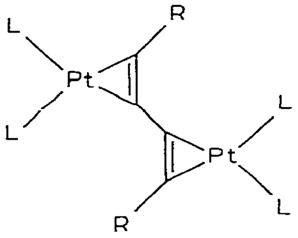
Complex		$\nu(C{\equiv}C)$ [a]	Chemical shifts and coupling constants [b]
I	$[Pt(PhC_4Ph)(PPh_3)_2]$	2170s, 1725s	—27.5 [c] (J(PPt) 3399 and 3618; ^2J(PP) 27).
II	$[Pt_2(PhC_4Ph)(PPh_3)_4]$	1780w(br), 1682m(br)	—26.8 and —28.5 (^1J(PPt) 3493 and 3481; ^4J(PPt) 34; ^2J(PP) 34; ^5J(PP) 10 and <2).
III	$[Pt(PhC_4Ph)(PMePh_2)_2]$	2140m, 1697m(br)	—5.2 and —4.7 (J(PPt) 3545 and 3268).
IV	$[Pt_2(PhC_4Ph)(PMePh_2)_4]$	1781m, 1669m	—4.6 and —4.2 (^1J(PPt) 3315 and 3498; ^2J(PP) 34; ^5J(PP) 5).
V	$[Pt(MeC_4Me)(PPh_3)_2]$	2205w, 1765m [d]	—28.5 and —30.4 (J(PPt) 3634 and 3409; J(PP) 37).
VI	$[Pt_2(MeC_4Me)(PPh_3)_4]$	1719m	—28.5 and —32.5 (^1J(PPt) 3530 and 3481; ^4J(PPt) 64; ^2J(PP) 45; ^5J(PP) 15 and <2).
VII	$[Pt_2(HC_2CH_2CH_2C_2H)(PPh_3)_4]$	1714m(br)	—29.6 and —32.1 (J(PPt) 3484 and 3645; J(PP) 43).

[a] Nujol mull, cm^{-1}. [b] ^{31}P (^{1}H-decoupled), chemical shifts in δ ppm (rel. H_3PO_4 external) measured in C_6D_6, coupling constants in Hz. [c] For the two non-equivalent nuclei the chemical shifts are coincident. [d] Lit. [7] 2205 and 1760 cm^{-1}.

a "free" C≡C group. The acetylene by itself shows a weak C≡C stretch at 2142 cm^{-1} in the infrared spectrum. The ^{31}P NMR spectrum of II is of the $[AB]_2$ or AA′BB′ type (Table 1), and is in accord with the structure proposed. Attempts to add a third $[Pt(PPh_3)_2]$ group to II via addition of the ethylene complex, to give a bridged-complex of type B (Fig. 1), failed. Only unreacted starting material was recovered.



(I) L = PPh_3 , R = Ph
(III) L = $PMePh_2$, R = Ph
(V) L = PPh_3 , R = Me



(II) L = PPh_3 , R = Ph
(IV) L = $PMePh_2$, R = Ph
(VI) L = PPh_3 , R = Me

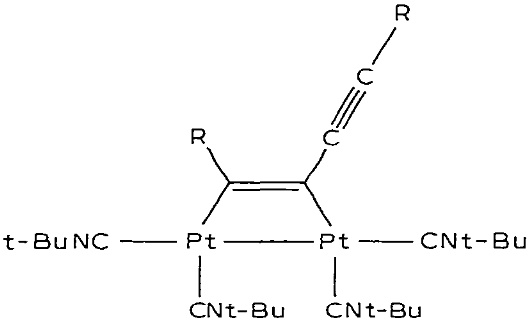
Reaction of $[Pt(C_2H_4)(PMePh_2)_2]$ with 1,4-diphenylbuta-1,3-diyne in a 1/1 ratio gave complex III, structurally analogous to I. If this reaction is carried out using a 2/1 molar ratio of $[Pt(C_2H_4)(PMePh_2)_2]$ to PhC_4Ph the di-platinum complex IV is formed. Again, as in the conversion of I into II, in forming complex IV the second platinum atom coordinates with the "free" acetylene group, rather than yielding a [$Pt_2(\mu_2\text{-}PhC{\equiv}CC_2Ph)L_4$] structure, as found in [$Pt_2(\mu_2\text{-}PhC{\equiv}CPh)(PMe_3)_4$] [6]. The ^{31}P NMR spectra (Table 1) of compounds III and IV, showing two resonances, are in accord with the indicated structures.

The di-acetylene hexa-2,4-diyne was similarly found to react with [$Pt(C_2H_4)(PPh_3)_2$] in two stages giving the mono- and di-platinum complexes V and VI, respectively. As mentioned earlier, compound V was first prepared by Roundhill et al. [7] via a different route. As in the synthesis of II and IV, the formation of VI is accompanied by the disappearance from the infrared spectrum of a band (2205 cm^{-1}) corresponding to an un-coordinated acetylene group. Interestingly, complex VI could not be obtained by the reduction of [$PtCl_2(PPh_3)_2$] in the presence of MeC_4Me [7], reflecting the higher reactivity of our systems based on platinum(0).

An interesting feature of the infrared spectra of the di-platinum complexes II and IV is the appearance of two bands in the region for a metal-coordinated acetylene group (Table 1). This perhaps suggests the presence of isomers, which could conceivably result from restricted rotation about the PhC_2—C_2Ph bonds, due to the bulky phenyl substituents. Some support for this suggestion comes from the observation of only one such band (1719 cm^{-1}) in the spectrum of VI, where phenyl groups have been replaced by methyl. Moreover, reaction of [$Pt(C_2H_4)(PPh_3)_2$] with hexa-1,5-diyne ($\nu(C{\equiv}C)$ 2105 cm^{-1}) gave [$Pt_2(\mu\text{-}HC{\equiv}C(CH_2)_2C{\equiv}CH)(PPh_3)_4$] (VII), a compound which also showed in its infrared spectrum only one coordinated acetylene band (Table 1). In this complex the two [$Pt(PPh_3)_2$] groups and the two acetylene linkages are well separated by the methylene groups. A notable feature of the reaction of [$Pt(C_2H_4)(PPh_3)_2$] with hexa-1,5-diyne is that even when a large excess of the acetylene is employed only the di-platinum complex VII is formed, there being no evidence for compounds corresponding to I, III or V.

We have also investigated reactions of the reactive cluster complex [$Pt_3(CN\text{-}t\text{-}Bu)_6$] [8] with the di-acetylenes $RC{\equiv}CC{\equiv}CR$ (R = Ph or Me). The tri-platinum complex acts as a source of [$Pt(CN\text{-}t\text{-}Bu)_2$] groups in a variety of reactions including those with acetylenes [9] and homo-acetylenes [10].

The infrared spectra of the products [$Pt_2(RC_4R)(CN\text{-}t\text{-}Bu)_4$] from 1,4-diphenylbuta-1,3-diyne and hexa-2,4-diyne showed the absence of a band near 1700 cm^{-1} indicative of an η^2-bonded acetylenemetal group, as found in complexes I—VII. Moreover, the ^1H NMR spectrum of [$Pt_2(PhC_4Ph)(CN\text{-}t\text{-}Bu)_4$] (VIII) showed three t-Bu resonances (rel. int. 18/9/9). These properties do not accord with molecular structures like II, IV and VI. Recently, di-platinum mono-acetylene complexes [$Pt_2(PhC_2Ph)(1,5\text{-}C_8H_{12})_2$] and [$Pt_2(RC_2R)(CN\text{-}t\text{-}Bu)_4$] (R = C_6F_5 or p-$MeOC_6F_4$) have been discovered [11] in which the acetylene bridges the two platinum atoms as in C (Fig. 1). These compounds, like VIII and IX, show no bands in their infrared spectra near 1700 cm^{-1}. To confirm the diplatinacyclobutene structures, complex VIII was prepared with isocyanide ligands labelled at the contact carbon atoms (t-Bu-$N^{13}C$) and ^{13}C NMR studies were carried out. The spectrum showed three resonances for the ligated carbon atoms of the four isocyanide ligands. A signal at δ 147.5 ppm ($^1J(PtC)$ 1131 and 1064 Hz) can be assigned to the two isocyanide ligands *trans* to the two



(VIII) R = Ph

(IX) R = Me

carbon atoms of the coordinated acetylene group. These t-BuNC groups are in an essentially similar environment and show no satellite peaks arising from ^2J(PtC) coupling because of the *cis*-PtPtCN-t-Bu configuration. The two other resonances observed at δ 140.7 ppm (^1J(PtC) 1088; ^2J(PtC) 314 Hz) and at 139.6 ppm (^1J(PtC) 1074; ^2J(PtC) 286 Hz) are attributable to a *trans*-t-BuNCPtPt configuration (VIII), resulting in the appearance of satellites corresponding to two bond ^{195}Pt—^{13}C coupling.

Experimental

General

All operations were carried out under dry oxygen-free nitrogen in Schlenk tubes. Light petroleum refers to the fraction b.p. 40—60°C. Hexa-2,4-diyne was obtained from 1,4-dichlorobut-2-yne [12]. t-Butyl isocyanide, approximately 15% enriched in t-BuN^{13}C, was prepared as follows. Labelled Na^{13}CN (0.5 g) and unlabelled NaCN (2.0 g) in water (20 ml) were well stirred with a slight excess of aqueous silver nitrate containing a few drops of concentrated nitric acid. The silver cyanide produced was filtered off, dried at 100°C and added to t-BuI (9 g) in dichloromethane (20 ml). The mixture was shaken for a minimum of 1 h. The yellow precipitate of the complex [AgI(CN-t-Bu)] so produced was shaken with KCN (3 eq.) in water (20 ml). Two colourless layers formed, and the t-BuNC contained in the dichloromethane layer was recovered by distillation.

Infrared spectra were recorded in Nujol on a Perkin—Elmer 457 spectrometer. ^{1}H-Decoupled ^{31}P and ^{13}C NMR spectra were obtained with a JEOL PFT-100 Fourier transform spectrometer using a ^{2}H lock. ^{13}C chemical shifts are relative to internal Me_4Si, positive values indicating signals to high frequency of the reference. For ^{31}P data see Table 1. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer. Analytical and other data for new compounds are given in Table 2.

Syntheses of [Pt(C_2H_4)L_2] (L = PPh_3 or $PMePh_2$) from [Pt(1,5-C_8H_{12})$_2$]

Typically, light petroleum (10 ml) was cooled to 0°C and saturated with

TABLE 2

MELTING POINTS, COLOUR AND ANALYSES

Compound	M.p. [a] (°C)	Colour	Analysis found (calcd.) (%)	
			C	H
I	212	cream	67.6 (67.7)	4.4 (4.6)
II	177	yellow	64.2 (64.4)	4.5 (4.3)
III	99	yellow	63.1 (63.2)	4.7 (4.5)
IV	174	cream	58.5 (58.6)	4.5 (4.5)
V	140	pale yellow	63.8 (63.2)	4.7 (4.6)
VI	168	yellow	62.1 (61.7)	4.6 (4.4)
VII	174	white	61.5 (61.7)	4.8 (4.4)
VIII [b]	146	brown	46.7 (46.7)	5.2 (5.0)
IX [c]	—	dark brown	38.3 (39.0)	5.1 (5.3)

[a] Generally occurs with decomposition. [b] N, 5.8 (6.1). [c] N, 6.8 (7.0).

ethylene. Bis(cycloocta-1,5-diene)platinum (206 mg, 0.5 mmol) was added, and the mixture stirred under ethylene until a clear pale yellow solution was obtained. A stoichiometric amount (262 mg, 1 mmol) of triphenylphosphine was then added, and the ethylene source exchanged for nitrogen. The mixture was then stirred at room temperature for ca. 1 h, during which time $[Pt(C_2H_4)(PPh_3)_2]$ precipitated in essentially quantitative yield. The complex $[Pt(C_2H_4)(PMePh_2)_2]$ was similarly prepared, using a hexane solution of $PMePh_2$ of known concentration.

Reactions of $[Pt(C_2H_4)L_2]$ with di-acetylenes

(a) Mono-platinum compounds. A sample of $[Pt(C_2H_4)(PPh_3)_2]$ (0.33 mmol), washed with light petroleum (3 × 5 ml) to remove cyclooctadiene, was suspended in light petroleum and PhC_4Ph (67 mg, 0.33 mmol) was added. The mixture was stirred for 16 h, filtered, and the precipitate washed with solvent (3 × 5 ml) before drying by pumping on a vacuum line to afford $[Pt(PhC_4Ph)(PPh_3)_2]$ (I) (254 mg, 83%). IR spectrum (cm^{-1}): 3060w(br), 2170s, 1725s, 1715(sh), 1588s, 1565w, 1479s, 1436s, 1305w(br), 1193(sh), 1179m, 1170(sh), 1159m, 1151(sh), 1094s, 1065m, 1026m, 999m, 918w, 902w, 848w(br), 824m, 751s, 768s, 748s, 705(sh), 699vs, 619w, 570w, 554w, 540s, 526vs, 518vs, 450w, 449s, 438w, 419vw.

1,4-Diphenylbuta-1,3-diyne (51 mg, 0.25 mmol) was added to $[Pt(C_2H_4)(PMePh_2)_2]$ (0.25 mmol) and the mixture stirred (20 h) at room temperature. The yellow precipitate was removed and washed (4 × 5 ml) with light petroleum and dried on a vacuum line to give $[Pt(PhC_4Ph)(PMePh_2)_2]$ (III) (90 mg, 45%). IR spectrum (cm^{-1}): 3040(br), 2140m, 1697m(br), 1585m, 1570(sh), 1479(m), 1430m, 1303w(br), 1280w, 1185w(br), 1151w, 1099m, 1074w, 1022w, 909w, 891(sh), 886s, 881(sh), 842w, 761m, 754m, 750m, 736m, 727m, 698s, 692m, 532m, 510m, 500(sh), 490w, 480(sh), 449w, 419w. ^1H NMR spectrum ($CDCl_3$): τ 2.9 (30H, Ph), 8.14 (d, 3H, Me, J(PtH) 28; J(PH) 8 Hz) and 8.32 (d, 3H, Me).

Hexa-2,4-diyne (81 mg, ca. 1 mmol) was added to a suspension of $[Pt(C_2H_4)$-

$(PPh_3)_2]$ (0.5 mmol) at room temperature and the mixture stirred for 3.5 h. The precipitate so obtained was washed with light petroleum (4 × 5 ml) and dried to give $[Pt(MeC_4Me)(PPh_3)_2]$ (V) (280 mg, 70%). IR spectrum (cm^{-1}): 3052w, 2205w, 1765m, 1580m, 1568(sh), 1468s, 1430s, 1305w(br), 1263w, 1180m, 1153w, 1091s, 1082(sh), 1068w, 1027m, 998w, 866(sh), 842w(br), 752s, 748s, 703(sh), 692s, 618w, 541s, 519(sh), 511s, 455m, 430s, 418(sh). ^1H NMR spectrum (C_6D_6): τ 2.2—3.2 (30H, Ph), 7.8 (3H, Me, *J*(PtH) 8; *J*(PH) 38 Hz) and 8.4 (3H, Me, *J*(PtH) 4; *J*(PH) 18 Hz).

(b) Di-platinum compounds. Complex I (235 mg, 0.25 mmol) was added as a powder to $[Pt(C_2H_4)(PPh_3)_2]$ (0.25 mmol) in light petroleum (15 ml). The mixture was stirred at room temperature (16 h), filtered, and the precipitate washed with light petroleum (5 ml) and dried in vacuo to give $[Pt_2(PhC_4Ph)(PPh_3)_4]$ (II) (320 mg, 78%), recrystallized from toluene/petrol at —20°C. IR spectrum (cm^{-1}): 3050w, 1780w(br), 1682m(br), 1585m, 1569w, 1479s, 1436s, 1305w(br), 1158w, 1130w, 1094s, 1069w, 1029m, 1000w, 916w, 846w, 757s, 750(sh), 745s, 700s, 616w(br), 541s, 525s, 512s, 454w, 421w.

1,4-Diphenylbuta-1,3-diyne (51 mg, 0.25 mmol) was added to a stirred suspension of $[Pt(C_2H_4)(PMePh_2)_2]$ (0.5 mmol) in hexane and the mixture was stirred for 22 h at room temperature. The precipitate obtained was washed (4 × 5 ml) with light petroleum and dried in vacuo to give $[Pt_2(PhC_4Ph)(PMePh_2)_4]$ (IV) (225 mg, 64%), recrystallized from toluene/light petroleum at —20°C. IR spectrum (cm^{-1}): 3050w, 1781m, 1669m, 1585m, 1570(sh), 1479s, 1439s, 1309w(br), 1155w(br), 1099m, 1068w, 1027w, 889s, 875s, 845s, 768w, 750m, 745(sh), 725s, 699s, 692(sh), 514m, 506m, 490w, 458(sh), 449m, 441(sh). ^1H NMR spectrum ($CDCl_3$): τ 2.5—3.5 (50H, Ph), 8.28 and 8.38 (12H, Me, *J*(PtH) 28 Hz).

The compound $[Pt_2(MeC_4Me)(PPh_3)_4]$ (VI) (190 mg, 83%) was prepared from $[Pt(MeC_4Me)(PPh_3)_2]$ (V) (120 mg, 0.15 mmol) in light petroleum (10 ml) by adding $[Pt(C_2H_4)(PPh_3)_2]$ (110 mg, 0.15 mmol) and stirring for 3 to 4 h. IR spectrum (cm^{-1}): 3050w, 1719m, 1582w, 1569w, 1479s, 1432s, 1308w(br), 1263w(br), 1181m, 1179(sh), 1159w, 1097s, 1068w, 1058(sh), 1028m, 998w, 970w, 950w, 930w(br), 918w, 851w, 843w, 758m, 746s, 700s(br), 620w, 541s, 527s, 517s, 500s, 452m, 440(sh), 429m, 415(sh).

Complex $[Pt_2\{HC_2(CH_2)_2C_2H\}(PPh_3)_4]$ (VII) (290 mg, 76%) was prepared from $[Pt(C_2H_4)(PPh_3)_2]$ (0.5 mmol) and a four-fold excess of hexa-1,5-diyne (143 mg, 1.8 mmol) by stirring in light petroleum at room temperature for 2 h. IR spectrum (cm^{-1}): 3065(sh), 3045w, 1714m(br), 1580w, 1568w, 1478s, 1430s, 1358w, 1177m, 1156m, 1098(sh), 1092s, 1056w, 1027m, 998w, 964w, 864m, 849m, 842(sh), 758s, 744s, 693vs, 620w, 578(sh), 569w, 562vs, 545s, 500s, 452m, 438w, 427(sh), 417m.

Reactions of $[Pt_3(CN\text{-}t\text{-}Bu)_6]$ with 1,4-diphenylbuta-1,3-diyne and hexa-2,4-diyne

1,4-Diphenylbuta-1,3-diyne (50 mg, 0.25 mmol) was added to $[Pt_3(CN\text{-}t\text{-}Bu)_6]$ (180 mg, 0.17 mmol) suspended in light petroleum (10 ml) and the mixture stirred at room temperature for 16 h. The tan precipitate was filtered, washed (4 × 8 ml) with solvent, and dried in vacuo to give $[Pt_2(PhC_4Ph)(CN\text{-}t\text{-}Bu)_4]$ (VIII) (170 mg, 73%). IR spectrum (cm^{-1}): 2145vs(br), 2025(sh) [ν(NC)], 1582w, 1229w, 1203s(br), 755m, 727(sh), 720w, 694w, 590w, 526(sh), 509w(br).

^{1}H NMR spectrum (acetone-d_6): τ 2.76 (10H, Ph), 8.4 (18H, Me), 8.54 (9H, Me) and 8.7 (9H, Me).

The compound $[Pt_2(MeC_4Me)(CN\text{-}t\text{-}Bu)_4]$ (IX) (88 mg, 33%) was similarly prepared from MeC_4Me (26 mg, 0.34 mmol) and $[Pt_3(CN\text{-}t\text{-}Bu)_6]$ (240 mg, 0.22 mmol) in light petroleum (5 ml). The complex can be recrystallized from acetone/petrol at −20°C. IR spectrum (cm^{-1}): 2150s(br) [ν(NC)], 1259w, 1231w, 1200m(br), 805w(br), 721w, 513w(br). ^{1}H NMR spectrum (acetone-d_6): τ 8—9 (m, Me).

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