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OXIDATIVE ADDITION AND INSERTION REACTIONS OF CYCLIC ALKYNE-PLATINUM(0) COMPLEXES

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Summary

The reactions of various alkyne-platinum(0) complexes with methyl iodide and with iodine have been studied. The 3-hexyne complex $Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$ gives alkyne-free oxidative addition products $PtI(CH_3)(PPh_3)_2$ and $PtI_2(PPh_3)_2$ exclusively. In contrast, the strained cyclic alkyne complexes $Pt(C_6H_8)(PPh_3)_2$, $Pt(C_7H_{10})(PPh_3)_2$, $Pt(C_6H_8)(dppe)$ and $Pt(C_7H_{10})(dppe)$[†] react with methyl iodide to give mainly 2-methylcycloalkenylplatinum(II) complexes, *e.g.* $PtI(C_6H_8CH_3)(PPh_3)_2$, formed by electrophilic attack on the metal-alkyne bond. Iodine reacts similarly with $Pt(C_6H_8)(PPh_3)_2$ and $Pt(C_7H_{10})(PPh_3)_2$ to give 2-iodocycloalkenylplatinum(II) complexes but, in the case of the corresponding dppe complexes, $PtI_2(dppe)$ is the main product. The insertion reaction of methyl iodide with $Pt(C_6H_8)(PPh_3)_2$ proceeds *via* an oxidative addition intermediate $PtI(CH_3)(C_6H_8)(PPh_3)_2$ which can be isolated. Trifluoromethyl iodide reacts with $Pt(C_6H_8)(PPh_3)_2$ to give a 2-iodocyclohexenyl complex $Pt(CF_3)(C_6H_8I)(PPh_3)_2$ and with

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[†] C_6H_8 = cyclohexyne; C_7H_{10} = cycloheptyne; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$.

$Pt(C_7H_{10})(PPh_3)_2$ to give $PtI(CF_3)(PPh_3)_2$. ^{31}P NMR data are given and discussed.

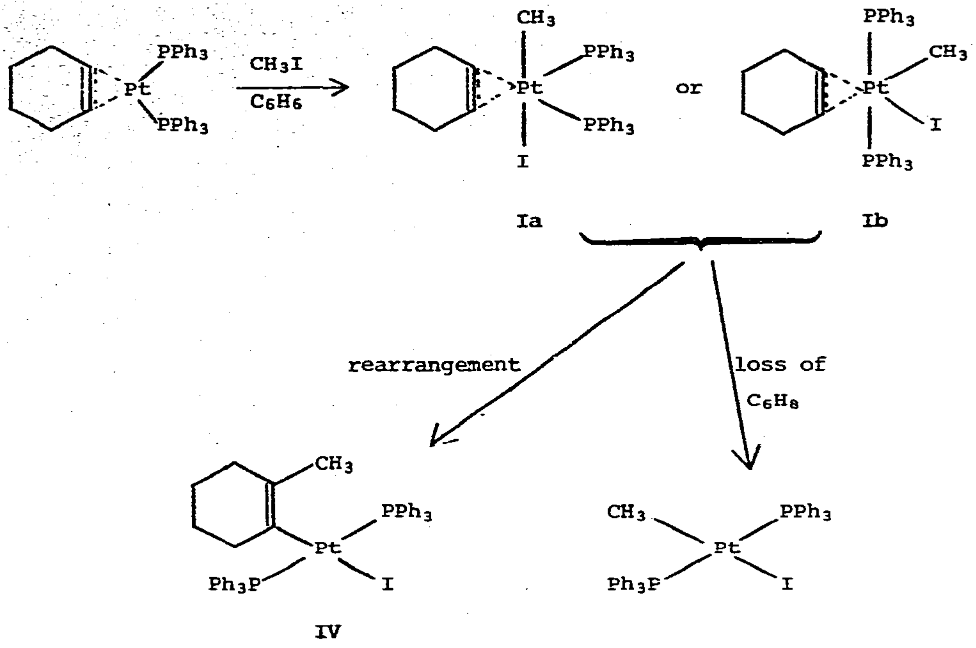
Introduction

Platinum(0) complexes of the short-lived small ring alkynes cyclohexyne and cycloheptyne are much more stable with respect to loss of the alkyne than are the analogous complexes of acyclic alkynes [1]. They might therefore be expected to undergo oxidative additions at the metal atom and insertions into the metal-alkyne bond without losing the alkyne unit. Examples of both types of reaction are reported in this paper.

Results

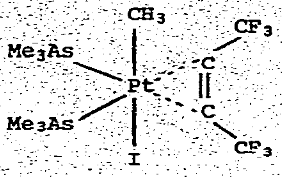
Methyl iodide reacts with the cyclohexyne complex $Pt(C_6H_8)(PPh_3)_2$ in benzene to give a colourless crystalline solid which we formulate as an oxidative addition product $PtI(CH_3)(C_6H_8)(PPh_3)_2$, I. The band at 1721 cm^{-1} due to '$\nu(C\equiv C)$' in $Pt(C_6H_8)(PPh_3)_2$ is absent from the spectrum of I, but a definitive assignment of $\nu(C\equiv C)$ could not be made. The ^{1}H NMR spectrum in CD_2Cl_2 shows a high-field triplet at δ -0.71 ppm with ^{195}Pt satellites [^3J(P-H) 6 Hz, ^2J(Pt-H) 46 Hz] which must be assigned to a Pt-CH_3 group cis to two equivalent triphenylphosphine ligands, and the $^{31}P\{^1H\}$ NMR spectrum shows one 1:4:1 triplet [J(Pt-P) 3270 Hz], confirming that the triphenylphosphine ligands are equivalent. Two structures, Ia and Ib (Scheme 1), are consistent with these data. We favour Ib because the cyclohexyne methylene resonances consist of four distinct complex multiplets, hence all four CH_2 groups are inequivalent. In contrast, $Pt(C_6H_8)(PPh_3)_2$ shows only two CH_2 multiplets in its ^{1}H NMR spectrum [1], and Ia would be expected to show a similar pattern. Attempts to identify the methylene ^{13}C resonances were unsuccessful.

The magnitude of $^2J(Pt-CH_3)$ in I is similar to that found for CH_3 trans to CH_3 in octahedral methylplatinum(IV) complexes (*ca.*

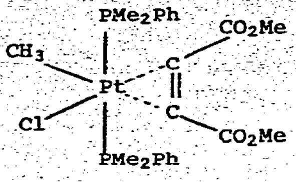


Scheme 1. Reaction of CH_3I with $Pt(C_6H_8)(PPh_3)_2$

44 Hz) and is considerably less than that for CH_3 trans to iodine (*ca.* 70 Hz) or tertiary phosphine (*ca.* 55—60 Hz) [2]. The only platinum(II) complexes which contain trans-methyl groups, $Li_2Pt(CH_3)_4$ and $Li[Pt(CH_3)_3PPh_3]$, also have $^2J(Pt\text{-}CH_3)$ values below 50 Hz [3], whereas the values for CH_3 trans to iodine or tertiary phosphine in planar platinum(II) complexes are only slightly lower than the values given above for octahedral platinum(IV) complexes. Thus, assuming that cyclohexyne can be regarded as a bidentate dicarbanionic ligand, the magnitude of $^2J(Pt\text{-}CH_3)$ in I indicates CH_3 to be trans to one of the cyclohexyne carbon atoms, in agreement with structure Ib. However, since $J(Pt\text{-}P)$ in I is far above the range expected for octahedral platinum(IV) complexes containing trans-tertiary phosphines [1850—2000 Hz] [4], it may be better to consider I as a five-coordinate μ-alkyne-platinum(II) complex than as a six-



II



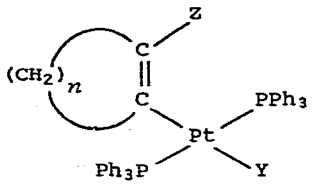
III

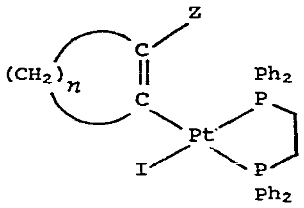
coordinate platinacyclopropene complex. Examples of the former are known, *e.g.* II and III, in which the $^{2}J(\text{Pt–CH}_3)$ values are 65.8 Hz and 57 Hz respectively [5,6].

If the reaction between $\text{Pt(C}_6\text{H}_8\text{)(PPh}_3\text{)}_2$ and methyl iodide is carried out in dichloromethane at room temperature over a 24 h period, or in refluxing dichloromethane or dichloromethane/ethanol for 3 h, a complex IV isomeric with I can be isolated. In addition to three cyclohexyne CH_2 multiplets in a ratio of 1:1:2, the ^{1}H NMR spectrum of IV has a methyl singlet at δ 1.49 with ^{195}Pt satellites; the chemical shift, the small value of J(Pt–H) (12 Hz), and the absence of ^{31}P coupling show that this cannot be due to a methyl group attached to platinum. The IR spectrum of IV shows a vinyl $\nu(C{=}C)$ absorption at 1615 cm^{-1}, hence IV is reasonably formulated as a 2-methylcyclohexenylplatinum(II) complex $\text{PtI(C}_6\text{H}_8\text{CH}_3\text{)(PPh}_3\text{)}_2$ derived by formal insertion of the methyl group into the platinum-alkyne bond of I. The $^{31}P\{^{1}H\}$ NMR spectrum of IV shows a singlet with ^{195}Pt satellites [J(Pt–P) 3270 Hz] consistent with mutually trans-triphenylphosphine ligands, *cf.* *trans*-$\text{PtCl(CH}_3\text{)(PMePh}_2\text{)}_2$, which has a J(Pt–P) value of 3028 Hz [7]; in analogous compounds, J(Pt–P) tends to increase as alkyl groups on phosphorus are replaced by aryl groups [8].

A solution of I in $CDCl_3$ decomposes over a 24 h period to give IV (*ca.* 85%) and *trans*-$\text{PtI(CH}_3\text{)(PPh}_3\text{)}_2$ (*ca.* 15%), identified by its characteristic 1:4:1 triplet of triplets due to Pt–CH_3. The fate of the eliminated cyclohexyne has not been determined. ^{1}H NMR monitoring of the reaction between Pt(C_6H_8)(PPh_3)$_2$ and methyl iodide in $CDCl_3$ showed that the oxidative addition product I is formed rapidly in the first step, and this then decays to give IV and *trans*-PtI(CH_3)(PPh_3)$_2$. The oxidative addition in C_6D_6, monitored by ^{1}H NMR, has a second order rate constant k_2 at 28 °C of 2.2×10^{-5} $mol^{-1} \ell sec^{-1}$, which is slower than the value of 3.9×10^{-3} $mol^{-1} \ell sec^{-1}$ for the addition of methyl iodide to IrCl(CO)(PPh_3)$_2$ in benzene at 30 °C [9].

Reaction of methyl iodide with Pt(C_6H_8)(dppe) in benzene at room temperature gives directly the 2-methylcyclohexenyl insertion product PtI($C_6H_8CH_3$)(dppe), V, the methyl resonance of which shows no resolvable ^{195}Pt satellites. The IR spectrum of V shows a low intensity vinyl ν(C═C) band at 1615 cm^{-1} and the $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets, each with ^{195}Pt satellites. The





IV $n = 4$, Y = I, Z = CH_3

VI $n = 5$, Y = I, Z = CH_3

VIII $n = 4$, Y = Z = I

X $n = 5$, Y = Z = I

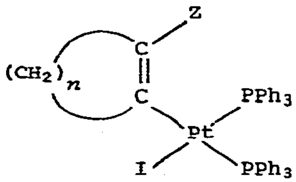
XIII $n = 4$, Y = CF_3, Z = I

V $n = 4$, Z = CH_3

VII $n = 5$, Z = CH_3

XI $n = 4$, Z = I

XII $n = 5$, Z = I



IX $n = 4$, Z = I

TABLE I. ^{31}P NMR DATA[a]

Complex	δ_P	J_{Pt-P}
$Pt(C_6H_8)(PPh_3)_2$	29.3(28.5)[b]	3409(3430)
$Pt(C_7H_{10})(PPh_3)_2$	29.4[c]	3420
$Pt(C_6H_8)(dppe)$	50.9(50.9)	3123(3152)
$Pt(C_7H_{10})(dppe)$	47.0	3058
$Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$[b]	29.1	3447
$PtI(CH_3)(C_6H_8)(PPh_3)_2$ (I)[b]	27.4	3320
trans-$PtI(C_6H_8CH_3)(PPh_3)_2$ (IV)[c]	22.0(21.9)	3270(3260)
$PtI(C_6H_8CH_3)(dppe)$ (V)	36.5	1551
	35.5	4270
trans-$PtI(C_7H_{10}CH_3)(PPh_3)_2$ (VI)	20.3	3350
$PtI(C_7H_{10}CH_3)(dppe)$ (VII)	40.5[d]	1541
	39.0[e]	3924
trans-$PtI(C_6H_8I)(PPh_3)_2$ (VIII)	17.7	3324
cis-$PtI(C_6H_8I)(PPh_3)_2$ (IX)	10.2[d,f]	1678
	11.4[e,f]	4394
trans-$PtI(C_7H_{10}I)(PPh_3)_2$ (X)	14.7	3274
$PtI(C_6H_8I)(dppe)$ (XI)	34.1[d]	1724
	36.9[e]	[g]
trans-$Pt(CF_3)(C_6H_8I)(PPh_3)_2$ (XIII)	20.0[h]	3392
trans-$PtI(CF_3)(PPh_3)_2$	19.4[i]	2962
$PtI_2(dppe)$	45.9	3388

[a] Measured in CH_2Cl_2 at 32 °C except where noted. Chemical shifts (δ_P) are in ppm (±0.5) downfield (positive) from external 85% H_3PO_4, coupling constants J(Pt-P) are in Hz (±10). Peaks are singlets except where stated.

[b] Data in parentheses refer to C_6H_6 solution.

[c] Measured in C_6H_6.

[d] P trans to cycloalkenyl group.

[e] P trans to I.

[f] Doublet, ^2J(P-P) 17 Hz.

[g] Satellites could not be located.

[h] Quartet, J(P-F) 10.4 Hz.

[i] Quartet, J(P-F) 21 Hz.

J(Pt–P) values of 1550 Hz and 4270 Hz are as expected for phosphorus trans to σ-alkenyl and iodide respectively in *cis*-$PtX(CH_3)(PEt_3)_2$ [4] and PtXR(dppe) (R = CH_3 or 1-cyclohexenyl; X = various anions) [10].

Similarly, methyl iodide reacts with the cycloheptyne complexes $Pt(C_7H_{10})(PPh_3)_2$ and $Pt(C_7H_{10})$(dppe) in benzene to give directly the 2-methylcycloheptenylplatinum(II) complexes $PtI(C_7H_{10}CH_3)(PPh_3)_2$, **VI**, and $PtI(C_7H_{10}CH_3)$(dppe), **VII**, which are characterised by their IR, ^{1}H NMR and ^{31}P NMR spectra (Table I). In both cases, minor amounts (15—25%) of the products derived by loss of alkyne, *i.e.* *trans*-$PtI(CH_3)(PPh_3)_2$ and $PtI(CH_3)$(dppe) could be detected; **VI** could not always be isolated completely free from *trans*-$PtI(CH_3)(PPh_3)_2$.

Iodine reacts immediately with $Pt(C_6H_8)(PPh_3)_2$ in dichloromethane to give a colourless solution which shows in its $^{31}P\{^1H\}$ NMR spectrum two doublets, each with ^{195}Pt satellites [^2J(P–P) 17 Hz, J(Pt–P) 1678, 4394 Hz]. These peaks decay over a period of hours and are replaced by a singlet with ^{195}Pt satellites [J(Pt–P) 3324 Hz]. The species responsible for this resonance can be isolated; it shows a complex ^{1}H NMR pattern in the δ 1—3 ppm region but bands due to $\nu(C{=}C)$ or $\nu(C{\equiv}C)$ could not be located in the IR spectrum. Owing to the limited solubility of **VIII**, the methylene carbon resonances could not be located in the ^{13}C NMR spectrum. We tentatively formulate the complex as the 2-iodocyclohexenyl derivative *trans*-$PtI(C_6H_8I)(PPh_3)_2$, **VIII**, and suggest on the basis of the ^{31}P NMR data that the intermediate species is the corresponding cis isomer, **IX**. Alternative formulations of **VIII** and **IX** as isomeric oxidative addition products cannot be completely ruled out, but they seem unlikely in view of the results with methyl iodide and especially in view of the similarity of the values of J(Pt–P) for **IX** and PtXR(dppe). Iodine also reacts immediately with the cycloheptyne complex $Pt(C_7H_{10})(PPh_3)_2$ in dichloromethane solution to give a colourless solution which has the 1:4:1 triplet ^{31}P resonance [J(Pt–P) 3274 Hz] indicative of a species with mutually trans-triphenylphosphine ligands. The ^{1}H NMR spectrum of the product which crystallizes from the solution shows the presence of a C_7H_{10} fragment but, as in the case of VIII, the IR spectrum is uninformative. The complex is probably the 2-iodocycloheptenylplatinum(II) complex, *trans*-PtI(C_7H_{10}I)(PPh_3)$_2$, X, but the alternative formulation as an oxidative addition product again cannot be completely excluded.

In contrast with the behaviour of the triphenylphosphine complexes, iodination of Pt(C_6H_8)(dppe) and Pt(C_7H_{10})(dppe) leads predominantly to loss of alkyne. ^{31}P NMR spectroscopy shows the main product to be PtI$_2$(dppe) contaminated in each case by a compound which is probably the expected insertion product XI or XII.

Trifluoromethyl iodide reacts with Pt(C_6H_8)(PPh_3)$_2$ in dichloromethane at room temperature to give a colourless 1:1 adduct. The IR spectrum shows ν(CF) bands at 1082 and 963 cm^{-1} and the ^{19}F NMR spectrum shows a triplet with ^{195}Pt satellites [^3J(P–F) 10.4 Hz, ^2J(Pt–F) 366 Hz] indicating that the trifluoromethyl group is attached directly to platinum. The magnitude of ^2J(Pt–F) is considerably smaller than that observed for CF_3 trans to ligands such as tertiary phosphines, isocyanides, pyridine and 1,5-cyclooctadiene in platinum(II) complexes (600 — 700 Hz) [11], and suggests that CF_3 is trans to a ligand of high trans influence. On this basis the complex is believed to be a 2-iodocyclohexenyl complex, *trans*-Pt(CF_3)(C_6H_8I)(PPh_3)$_2$, XIII. The presence of trans-triphenylphosphine ligands is supported by the appearance of a quartet in the ^{31}P{^{1}H} NMR spectrum with ^{195}Pt satellites [J(Pt–P) 3392 Hz]. In contrast, trifluoromethyl iodide displaces cycloheptyne from Pt(C_7H_{10})(PPh_3)$_2$ to give *trans*-PtI(CF_3)(PPh_3)$_2$, identical with the product obtained using Pt(PPh_3)$_4$ in place of Pt(C_7H_{10})(PPh_3)$_2$ [12].

Discussion

The insertion reactions probably proceed *via* an oxidative addition intermediate similar to that isolated in the reaction of Pt(C_6H_8)(PPh_3)$_2$ with methyl iodide. This intermediate can either isomerize by transferring one of the added groups to the coordinated alkyne, or it can lose the alkyne (Scheme 1). The second alternative is observed exclusively in the additions of methyl iodide or iodine to the 3-hexyne complex Pt($C_2H_5C_2C_2H_5$)(PPh_3)$_2$, which give *trans*-PtI(CH_3)(PPh_3)$_2$ and PtI_2(PPh_3)$_2$ as the only metal-containing products. In view of the ready loss of alkyne from the initial complex, this result is not surprising but, even in additions to the much more stable cyclic alkyne complexes, loss of alkyne occurs to a greater or lesser extent. In general, cycloheptyne is more readily displaced than the more strained cyclohexyne, a trend which is particularly evident in the reactions of Pt(cyclic alkyne)(PPh_3)$_2$ with CF_3I. Loss of alkyne is also promoted by the presence of dppe in place of 2PPh_3, possibly as a consequence of steric hindrance in the presumed oxidative addition intermediate.

The insertions can be regarded as electrophilic attack on the coordinated alkynes, a view which accounts for the difference in behaviour of CF_3I and CH_3I with Pt(C_6H_8)(PPh_3)$_2$. Since the C-I bond of CF_3I is polarized in the opposite sense to that of CH_3I [13], it is the more positively charged iodine atom of CF_3I which migrates to the alkyne. Platinum(0) complexes of both cyclic and acyclic acetylenes are readily protonated to give σ-vinylplatinum(II) complexes [1,14,15,16] and coordinated hexafluoro-2-butyne in the complexes Pt($CF_3C_2CF_3$)(PR_3)$_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph) also undergoes electrophilic attack by mercuric chloride [17], but we know of no examples involving alkyl halides or halogens.

The fact that the oxidative addition intermediate can only be isolated in the case of Pt(C_6H_8)(PPh_3)$_2$ and methyl iodide may reflect in part the greater stability of the metal-cyclohexyne bond relative to the metal-cycloheptyne bond. It is also worth noting that five-coordinate platinum(II)-alkyne complexes of the type $PtXClL_2(ac)$ can only be isolated when $X = CH_3$, not when X = halide or CF_3 [5,6] presumably because the strongly electron-donating methyl group assists back donation to the coordinated alkyne.

We have suggested elsewhere [1] that the greater reactivity of platinum(0)-cyclohexyne complexes relative to the analogous cycloheptyne complexes can be accounted for by assuming some metallocyclopropene character in the metal-cyclohexyne bond. Any difference of this sort is not reflected in the Pt-P bonds. The magnitudes of J(Pt-P) in the cyclohexyne and cycloheptyne complexes are almost equal, and both are only marginally smaller than J(Pt-P) in $Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$. This is consistent with the near identity of Pt-P bond lengths in $Pt(C_6H_8)(PPh_3)_2$, $Pt(C_7H_{10})(PPh_3)_2$ and $Pt(PhC_2Ph)(PPh_3)_2$ [18,19]. The J(Pt-P) values for the dppe complexes are uniformly less than those for the triphenylphosphine complexes. Comparison of ^1J(Pt-C) values for these complexes would be of obvious interest, but we have been unable to locate the acetylenic carbon resonances in the ^{13}C NMR spectra.

Comparison of J(Pt-P) values in the appropriate platinum(II)dppe complexes shows that the NMR trans influences of 2-methylcyclohexenyl and 2-methylcycloheptenyl are very similar to those of cyclohexenyl and cycloheptenyl. However, the J(Pt-P) values for complexes IX, XI and XII indicate that 2.iodocyclohexenyl has somewhat lower trans influence, comparable with that of methyl, perhaps as a consequence of the electron-withdrawing effect of the iodine or because its steric bulk causes a lengthening of the Pt-C bond in the 2-iodocyclohexenyl complexes relative to the cyclohexenyl complexes.

Experimental

IR spectra were measured on a PE457 spectrometer calibrated with polystyrene, ^1H NMR spectra were obtained on JEOL MH-100

TABLE II. ANALYTICAL DATA AND MELTING POINTS

	Analysis found (calcd) (%)				
	C	H	P	I	M.p.
$PtI(CH_3)(C_6H_8)(PPh_3)_2$ (I)	54.6 (54.8)	4.3 (4.4)	6.0 (6.6)	13.35 (13.5)	164 – 165° (dec.)
$PtI(C_6H_8CH_3)(PPh_3)_2.0.4CH_2Cl_2$ (IV)^{a,b}	53.5 (53.5)	4.5 (4.2)	6.4 (6.4)	13.4 (13.0)	232 – 239° (dec.)
$PtI(C_6H_8CH_3)(Ph_2PCH_2CH_2PPh_2).C_6H_6$ (V)	51.8 (52.4)	4.7 (4.6)	7.4 (6.9)	14.2 (14.2)	205 – 209° (dec.)
$PtI(C_7H_{10}CH_3)(PPh_3)_2$ (VI)^{c}	52.4 (53.6)	4.5 (4.4)	6.2 (6.2)	12.8 (12.7)	218 – 220° (dec.)
$PtI(C_7H_{10}CH_3)(Ph_2PCH_2CH_2PPh_2)$ (VII)	49.7 (49.2)	4.4 (4.5)	7.3 (7.5)	14.4 (15.3)	180° (dec.)
$PtI(C_6H_8I)(PPh_3)_2.0.3C_6H_{14}$ (VIII)^{d}	48.8 (49.0)	4.0 (3.9(	5.7 (5.7)	23.5 (23.6)	209 – 211° (dec.)
$PtI(C_7H_{10}I)(PPh_3)_2.0.7C_6H_{14}$ (X)^{d}	50.3 (50.2)	4.6 (4.3)	5.7 (5.5)	22.4 (22.6)	darkens >150°
$Pt(CF_3)(C_6H_8I)(PPh_3)_2.C_6H_{14}$ (XIII)^{d}	54.2 (54.4)	4.5 (4.8)			160° (dec.; darkens >130°)

[a] %Cl found, 2.8; calcd, 2.8; presence of CH_2Cl_2 confirmed by ^1H NMR spectrum in $CDCl_3$.

[b] Mol.wt. (CH_2Cl_2): found, 957; calcd 942.

[c] In a second experiment, an inseparable 4:1 mixture of VI and $PtI(CH_3)(PPh_3)_2$ was obtained. *Anal.* Found: C, 54.2; H, 4.6; P, 6.6. Calcd: C, 54.4; H, 4.4; P, 6.6%.

[d] Presence of *n*-hexane evident from ^1H NMR spectrum.

or Varian HA-100 instruments using either TMS or, in the case of Pt-CH_3 resonances, dichloromethane as internal references. ^{19}F NMR spectra were measured on a JEOL C60 CW spectrometer at 56.4 MHz; fluorine chemical shifts δ_F are in ppm upfield from internal $CFCl_3$. $^{31}P\{^1H\}$ NMR spectra were measured at 24.3 MHz either on the JEOL C60 CW instrument or on a modified Bruker 3225 FT spectrometer linked to a PDP 11/40 data acquisition and processing computer. The modifications to the latter instrument include an external fluorine lock and multinuclear decoupling facilities. Microanalyses were carried out in the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University. ^{31}P NMR data are in Table I, analytical data are in Table II.

Preparations

Bis(triphenylphosphine)(3-hexyne)platinum(0), $Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$. This was prepared in 74% yield from *cis*-$PtCl_2(PPh_3)_2$ and 3-hexyne following the literature procedure for the corresponding diphenylacetylene complex [20].

Anal. Found: C, 63.8; H, 5.5; P, 7.4. Calc for $C_{42}H_{40}P_2Pt$: C, 62.9; H, 5.0; P, 7.4%. IR (Nujol) 1804 cm^{-1} [$\nu(C\equiv C)$]. ^1H NMR (C_6D_6) δ 1.05 (t, CH_3), 2.60 [m, CH_2, J(H-H) 7.3 Hz] *cf.* free 3-hexyne δ 0.90 (t, CH_3), 1.96 [q, CH_2, J(H-H) 8.0 Hz].

The compound decomposes slowly in benzene solution and much more quickly in chlorinated solvents. It cannot therefore be recrystallized satisfactorily, and the solid always smells of 3-hexyne.

Reactions of alkyne complexes with methyl iodide (1). A mixture of $Pt(C_6H_8)(PPh_3)_2$ (0.08 g, 0.1 mmol), methyl iodide (0.2 ml, *ca.* 30-fold excess) and benzene (5 ml) was heated under reflux for 3 h. Evaporation under reduced pressure gave a solid which, after recrystallization from benzene/*n*-hexane gave colourless crystalline *bis(triphenylphosphine)cyclohexyneiodomethylplatinum(II)*, $PtI(CH_3)(C_6H_8)(PPh_3)_2$, I, (0.062 g, 66%). NMR (CD_2Cl_2): δ 1.88, 1.62(4), 0.93 – 0.2(4) (complex multiplets, CH_2 of C_6H_8), − 0.71(3) [t with ^{195}Pt satellites, Pt-CH_3, J(P-H) 6, J(Pt-H) 46 Hz].

(2) A solution of I (0.047 g, 0.05 mmol) in dichloromethane (5 ml) and ethanol (2 ml) was heated under reflux for 3 h. Evaporation to dryness under reduced pressure and recrystallization of the solid residue from dichloromethane/ethanol gave colourless crystalline *bis(triphenylphosphine)iodo(2-methylcyclohexenyl)platinum(II)*, $PtI(C_6H_8CH_3)(PPh_3)_2$, IV, (0.03 g, 64%). IR (KBr) $\nu(C{=}C)$ 1631 cm^{-1} NMR (CD_2Cl_2): δ 1.49(3) [s with ^{195}Pt satellites, C-CH_3, J(Pt-H)

12 Hz] 1.76(2), 1.18(2), 0.38(4) (broad multiplets, CH_2 of C_6H_8). Monitoring of the Pt-CH_3 resonance of I in NMR spectrum showed that the isomerization I → IV was complete at *ca.* 32 °C over a period of 24 h in $CDCl_3$ or over a period of days in dichloromethane/ethanol. About 15% of *trans*-PtI(CH_3)(PPh_3)$_2$ was also formed; it was identified by its triplet resonance at δ 0.11 [^3J(P-H) 6 Hz] in $CDCl_3$.

(3) A mixture of Pt(C_6H_8)(dppe) (0.135 g, 0.2 mmol), methyl iodide (0.2 ml, *ca.* seven-fold excess) and benzene (5 ml) was heated under reflux for 2 h. Evaporation under reduced pressure gave a viscous oil which crystallized on addition of *n*-hexane. Recrystallization from benzene/*n*-hexane gave colourless crystalline *bis(1,2-diphenylphosphino)ethaneiodo(2-methylcyclohexenyl)platinum(II)*, PtI($C_6H_8CH_3$)(dppe).C_6H_6, V, (0.132 g, 84%). ^{1}H NMR (CD_2Cl_2) δ 1.96(3) (s, C-CH_3), 2.1–3(12) (overlapping complex multiplets, CH_2 of dppe and C_6H_8).

(4) A mixture of Pt(C_7H_{10})(PPh_3)$_2$ (0.105 g, 0.15 mmol), methyl iodide (0.2 ml, *ca.* 20-fold excess) and benzene (5 ml) was heated under reflux for 2 h. Work-up as described in *(3)* gave colourless crystalline *bis(triphenylphosphine)iodo(2-methylcycloheptenyl)platinum(II)*, PtI($C_7H_{10}CH_3$)(PPh_3)$_2$,VI. This sample was used for the ^{1}H NMR measurement, and the analytical sample was obtained from it in 62% yield by recrystallization from dichloromethane/ethanol, although some *trans*-PtI(CH_3)(PPh_3)$_2$ impurity often remained. IR (KBr) ν(C═C) 1615 cm^{-1}. NMR (CD_2Cl_2): δ 1.80(3) [s with ^{195}Pt satellites, C-CH_3, J(Pt-H) 12 Hz], 2.08(2), 1.33(3), 1.0–0.3(5) (complex multiplets, CH_2 of C_7H_{10}).

(5) A solution of Pt(C_7H_{10})(dppe) (0.107 g, 0.16 mmol) in benzene (10 ml) was treated with methyl iodide (0.5 ml, excess). The solution was set aside overnight and evaporated to dryness under reduced pressure without heating. The ^{1}H NMR spectrum of the residue in $CDCl_3$ showed complex multiplets in the range δ 1–3 ppm

and a weak doublet of doublets at δ 1.29 [*J*(P-H) 4.0, 7.0 Hz] due to a small amount of $PtI(CH_3)(dppe)$. The major product , *(1,2-bis(diphenylphosphino)ethane)iodo(2-methylcycloheptenyl) platinum(II)*, $PtI(C_7H_{10}CH_3)(dppe)$,VII, was obtained by recrystallisation from chloroform/*n*-hexane. Yield: 0.118 g (92%).

(6) Addition of a drop of methyl iodide to a solution of $Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$ (0.5 g, 0.06 mole) in C_6D_6 (5 ml) immediately gave *trans*-$PtI(CH_3)(PPh_3)_2$, identified by its characteristic methyl triplet with ^{195}Pt satellites in the ^1H NMR spectrum: δ (C_6D_6) 0.80 (CD_2Cl_2) 0.05 [^3J(P-H) 6.5 Hz, ^2J(Pt-CH_3) 76 Hz]. A similar reaction occurred over a period of hours on addition of methyl iodide to $Pt(PhC_2H)(PPh_3)_2$.

Reactions of alkyne complexes with iodine (1). A solution of $Pt(C_6H_8)(PPh_3)_2$ (0.111 g, 0.14 mmol) in *ca.* 0.5 ml of dichloromethane in an NMR tube was treated with iodine (0.035 g, 0.14 mmol) to give a colourless solution. The $^{31}P\{^1H\}$ NMR spectrum showed peaks assigned to *cis*-$PtI(C_6H_8I)(PPh_3)_2$,IX (Table I), but over a period of hours these were replaced by the peaks due to the *trans*-isomer VIII. The solution was evaporated to dryness and after recrystallization from dichloromethane/*n*-hexane gave colourless microcrystals of trans-*bis(triphenylphosphine)iodo(2-iodocyclohexenyl)platinum(II)*, $PtI(C_6H_8I)(PPh_3)_2.0.3C_6H_{14}$, VIII (0.119 g, 79%). The ^1H NMR spectrum showed overlapping complex multiplets in the region of δ 1—3 ppm.

(2) A solution of $Pt(C_7H_{10})(PPh_3)_2$ (0.155 g, 0.19 mmol) in *ca.* 0.5 ml of dichloromethane in an NMR tube was treated with iodine (0.0475 g, 0.19 mmol) to give a colourless solution. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet with ^{195}Pt satellites due to X, and this product slowly crystallized from solution. After recrystallization from dichloromethane/*n*-hexane, 0.139 g (65%) of trans-*bis(triphenylphosphine)iodo(2-iodocycloheptenyl)platinum(II)*,

$PtI(C_7H_{10}I)(PPh_3)_2.0.7C_6H_{14}$,X, was obtained. The ^1H NMR spectrum showed a complex pattern in the region of δ 0—3 ppm, and peaks due to $\nu(C{=}C)$ or $\nu(C\overset{\cdots}{=}C)$ could not be located in the IR spectrum.

(3) Both $Pt(C_6H_8)(dppe)$ and $Pt(C_7H_{10})(dppe)$ reacted immediately with one mole equivalent of iodine in dichloromethane, but the main product in both cases was $PtI_2(dppe)$, as shown by ^{31}P NMR spectroscopy. Weak peaks tentatively assigned to the expected product, **XI**, were observed in the case of $Pt(C_6H_8)(dppe)$ but, in the case of $Pt(C_7H_{10})(dppe)$, the only minor peak in addition to those of $PtI_2(dppe)$ was at δ_P 38.6 ppm, and its ^{195}Pt satellites were not observed.

(4) Addition of iodine (0.012 g, 0.047 mole) to a solution of $Pt(C_2H_5C_2C_2H_5)(PPh_3)_2$ (0.035 g, 0.044 mole) in benzene (5 ml) immediately gave an orange precipitate of *trans*-$PtI_2(PPh_3)_2$ quantitatively.

Reaction of alkyne complexes with trifluoromethyl iodide. (1) Trifluoromethyl iodide (*ca.* 10 mmol, excess) was condensed on to a solution of $Pt(C_6H_8)(PPh_3)_2$ (0.290 g, 0.36 mmol) in dichloromethane (2 ml) in a Carius tube and the mixture was set aside at room temperature for 3 d. Solvent was evaporated and the solid residue was recrystallized from dichloromethane/*n*-hexane to give 0.153 g (52%) of trans-*bis(triphenylphosphine)(2-iodocyclohexenyl)trifluoromethylplatinum(II)*, $Pt(CF_3)(C_6H_8I)(PPh_3)_2.C_6H_{14}$,XIII. IR (Nujol): 1082, 963 cm^{-1} [$\nu(CF)$]. ^1H NMR (CD_2Cl_2): overlapping multiplets in the region δ 1—3 ppm due to CH_2 of C_6H_8, CH_2 + CH_3 of *n*-hexane. ^{19}F NMR (CH_2Cl_2): δ_F 14.6 [t with ^{195}Pt satellites, ^3J(P-F) 10.4, ^2J(Pt-F) 366 Hz].

$Pt(C_6H_8)(dppe)$ did not react with trifluoromethyl iodide under similar conditions.

(2) A solution of $Pt(C_7H_{10})(PPh_3)_2$ (0.257 g, 0.32 mmol) in dichloromethane (*ca.* 5 ml) was treated with trifluoromethyl iodide

as described above. Large crystals which deposited over 10 d were identified as *trans*-$PtI(CF_3)(PPh_3)_2$ (0.139 g, 48%) from their IR spectra [12] and NMR spectra. ^{19}F NMR (CH_2Cl_2): δ_F 12.7 [t with ^{195}Pt satellites, $^3J(P-F)$ 21, $^2J(Pt-F)$ 700 Hz].

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