

Synthesis and Reactivity of Zerovalent Platinum Complexes of Short-Lived Cyclic Alkynes. Formation of Monomeric Platinum(II) Hydroxo-, Methoxo-, and σ -Carbon-Bonded Complexes by Oxidative Addition Reactions with Water, Methanol, and Activated Hydrocarbons and Catalysis of Hydration of Nitriles to Amides

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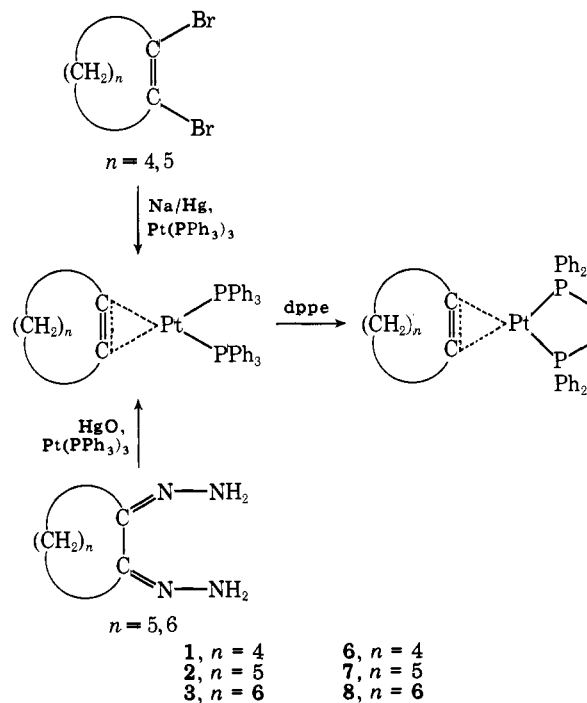
Abstract: The short-lived small-ring alkynes cyclohexyne and cycloheptyne (ac) can be trapped in the form of stable complexes of zerovalent platinum or palladium $M(ac)L_2$ [$M = Pt, Pd; L_2 = 2PPh_3$ or $Ph_2PCH_2CH_2PPh_2(dppe)$] from which the alkynes are not readily displaced by other unsaturated ligands. However, the cyclohexyne complex $Pt(C_6H_8)(PPh_3)_2$ (**1**) reacts with PF_3 to give $Pt(PF_3)_2(PPh_3)_2$ and with CO to give $Pt_2(CO)_2(PPh_3)_2(\mu-C_6H_8)$ (**11**). The two-step reaction of **1** with *tert*-butyl isocyanide gives initially $Pt(C_6H_8)(PPh_3)(t-BuNC)$ (**9**), and finally the insertion product $Pt[C(=NBu-t)C_6H_8](PPh_3)(t-BuNC)$ (**10**). The cyclic alkyne-platinum(0) complexes are readily protonated by HCl or CF_3CO_2H to give 1-cycloalkenylplatinum(II) complexes, e.g., $PtCl(C_6H_9)(PPh_3)_2$ (**12**). The cyclohexyne complexes differ from the cycloheptyne complexes in being protonated by a variety of weak protonic acids. Thus $Pt(C_6H_8)(dppe)$ (**6**) reacts with water or methanol to give stable, monomeric hydroxo- or methoxoplatinum(II) complexes $Pt(OR)(C_6H_9)(dppe)$ ($R = H$, **22**; $R = CH_3$, **23**) and with weak carbon acids such as nitromethane, acetonitrile, phenylacetone, acetone, and acetophenone to give functionalized alkyl cyclohexenylplatinum(II) complexes, e.g., $Pt(CH_2COCH_3)(C_6H_9)(dppe)$ (**28**) and $Pt(CH_2CN)(C_6H_9)(dppe)$ (**30**). Reaction of **6** with methyl ketones requires the presence of water and proceeds via the hydroxo complex **22**. Reaction of **1** or **6** with acetamide or benzamide affords *N*-amidoplatinum(II) complexes, e.g., $Pt(NHCOR)(C_6H_9)(dppe)$ ($R = CH_3$, **32**; $R = Ph$, **33**). Such complexes are also formed in the reactions of **1** or **6** with aqueous acetonitrile or benzonitrile in which the free amide is generated catalytically. The bonding in cyclic alkyne complexes is discussed in the light of their reactions, IR spectra, and structures. It is suggested that the cyclohexyne complexes may be best represented as metallocyclopropenes.

The simplest unsubstituted cyclic alkyne known in the free state is the eight-membered ring cyclooctyne. The smaller members of the series, such as cycloheptyne and cyclohexyne, have defied repeated attempts at synthesis owing to their reactivity, but their existence as short-lived intermediates has been established by trapping experiments and kinetic studies.¹ Recently, 3,3,7,7-tetramethylcycloheptyne has been isolated as a pure liquid which undergoes ready thermal dimerization.² The possibility of stabilizing small-ring acetylenes by complexing with transition metals was foreshadowed in the reported reaction of $Co_2(CO)_8$ with octafluoro-1,3-cyclohexadiene (1,3- C_6F_8) to give a complex $Co_2(CO)_6(C_6F_6)$ containing a bridging hexafluoro-1,3-cyclohexenyne ligand $C\equiv C-CF=CF-CF_2CF_2$.^{3,4} Since stable complexes $Pt(PPh_3)_2(ac)$ are formed by a wide range of acetylenes,^{5,6} it seemed worthwhile to try to trap short-lived acetylenes with $Pt(PPh_3)_3$. Following our preliminary report,⁷ we now describe in detail the preparation, properties, and reactions of small-ring alkyne-platinum(0) complexes.

Results

Routes to cyclic alkyne-platinum(0) complexes are outlined in Scheme I. The best method is the reaction of the 1,2-dibromocycloalkene with sodium amalgam in tetrahydrofuran containing $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$ at room temperature, which gives the colorless, crystalline cyclohexyne complex $Pt(C_6H_8)(PPh_3)_2$ (**1**) in 50–60% yield, and the similar cycloheptyne complex $Pt(C_7H_{10})(PPh_3)_2$ (**2**) in ca. 80% yield. **2** is also obtained in poor yield from mercuric oxide oxidation of 1,2-cycloheptanedione bis(hydrazone) in the presence of $Pt(PPh_3)_3$. Similar treatment of 1,2-cyclooctanedione bis(hydrazone) gives the cyclooctyne complex $Pt(C_8H_{12})(PPh_3)_2$ (**3**), which has been obtained independently by reaction of cyclooctyne with $Pt(PPh_3)_4$ ^{8a} or with $PtCl_2(PPh_3)_2$ in the presence of hydrazine.^{8b} An attempt to prepare the cy-

Scheme I. Preparation of Cyclic Alkyne-Platinum(0) Complexes



cloheptyne complex by reaction of 1,2-dibromocyclopentene with sodium amalgam in the presence of $Pt(PPh_3)_3$ was unsuccessful. The palladium(0) complexes $Pd(C_6H_8)(PPh_3)_2$ (**4**) and $Pd(C_7H_{10})(PPh_3)_2$ (**5**) can be prepared in ca. 25% yield by the reductive procedure using $Pd(PPh_3)_4$ in place of $Pt(PPh_3)_3$. These complexes are much less stable than their platinum analogues, and their chemistry will not be considered further here.

Single-crystal x-ray structural analyses of **1–3**⁹ confirm that the hydrocarbon ligands present are the cyclic alkynes, not the isomeric cyclic allenes. Attempts to displace the alkynes with 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂PPh₂(dppe), lead to replacement of the triphenylphosphine ligands and formation of the colorless, crystalline complexes Pt(C₆H₈)(dppe) (**6**), Pt(C₇H₁₀)(dppe) (**7**), and Pt(C₈H₁₂)(dppe) (**8**). The latter resemble **1–3** in being readily soluble in benzene, dichloromethane, chloroform, tetrahydrofuran, and carbon disulfide and almost insoluble in saturated hydrocarbons, ether, and alcohol. The IR spectra of the complexes show a strong band in the region of 1700–1800 cm⁻¹ (Table I) which is assigned to $\nu(\text{C}\equiv\text{C})$ modified by coordination. The ¹H NMR spectra generally show two groups of broad, complex methylene resonances, that at lower field being due to the CH₂ protons α to the coordinated triple bond. Owing to the broadness of the resonances, no ¹⁹⁵Pt satellites were observed.

The coordinated cyclic alkynes are much more resistant to displacement than are their acyclic counterparts. The mass spectra of **1** and **2** show parent ions in addition to the fragment [Pt(PPh₃)₂]⁺. **1–3** and **6–8** are air stable in solution for several weeks, whereas the 4-octyne complex Pt(PPh₃)₂(*n*-PrC₂Pr-*n*) loses alkyne in the solid state at room temperature and is dissociated in solution.^{8b} **1** is unaffected by diphenylacetylene, methyl propiolate, dimethyl acetylenedicarboxylate, carbon disulfide, and 2,2'-bipyridyl, while **2** is inert both toward these ligands and toward carbon monoxide and *tert*-butyl isocyanide (*t*-BuNC). However, a suspension of **1** in *n*-hexane reacts with *t*-BuNC at room temperature to give a colorless, diamagnetic substitution product Pt(C₆H₈)(PPh₃)(*t*-BuNC) (**9**), which shows two sets of α -CH₂ resonances in its ¹H NMR spectrum and a band at 1705 cm⁻¹ in its IR spectrum due to coordinated cyclohexyne. In benzene at room temperature **1** reacts with an excess of *t*-BuNC to give a pale yellow diamagnetic complex of empirical formula Pt(C₆H₈)(PPh₃)(*t*-BuNC)₂ in good yield which we formulate as the insertion product **10**. **10** is also obtained by treatment of **9** with *t*-BuNC. In the IR spectrum there is no band assignable to coordinated cyclohexyne, but there are bands at 1570 and 1601 cm⁻¹ due to " $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ ", and the ¹H NMR spectrum shows the presence of two different *tert*-butyl groups. Also consistent with the proposed structure is the bathochromic shift of $\nu(\text{CN})$ in **10** relative to **9**, which suggests an increase in the formal oxidation state of the metal. Although isocyanide insertions into metal-carbon σ bonds are well known,^{10–12} there is only one previous report¹³ of such an insertion into a metal-alkyne bond, viz., the reaction of aryl isocyanides with C₅H₅Co(PhC₂Ph)(PPh₃) to give insertion products such as (C₅H₅)(Ph₃P)-CoC(=NPh)-C(Ph)=C(Ph) and (C₅H₅)(PhNC)-CoC(=NPh)-C(Ph)=C(Ph)C(=NPh). The cycloaddition of isocyanides with diphenylacetylene catalyzed by nickel(0) complexes¹⁴ probably proceeds via intermediates similar to **10**. Further insertion of *t*-BuNC into the Pt-C σ bond of **10** is not observed; this inertness seems to be characteristic of platinum(II) σ alkyls,¹² since multiple insertions of isocyanides are well established in other systems.^{10,11,13,15}

In further contrast with the inertness of **2**, **1** reacts with carbon monoxide in boiling benzene to give a pale yellow, diamagnetic complex of empirical formula C₆H₈Pt₂(CO)₂(PPh₃)₂ in about 40% yield. The fate of the displaced cyclohexyne has not been determined. The IR spectrum exhibits two strong $\nu(\text{CO})$ bands suggestive of *cis* carbonyl groups and the ¹H NMR spectrum shows a pair of equally intense methylene resonances; hence the two "acetylenic" cyclohexyne carbon atoms probably are equivalent. These data, and the fact that the lower field methylene resonance shows ¹⁹⁵Pt satellites (*J*_{PtH} = 34 Hz), are consistent with the metal-metal bonded structure, **11**, which contains formal Pt(I); other examples of binuclear platinum(I) complexes have been reported re-

Table I. Selected IR and NMR Spectroscopic Data for Cyclic Alkyne Complexes

	$\nu(\text{C}\equiv\text{C})$, cm ⁻¹ ^a	α -CH ₂ (δ) ^b	Other CH ₂ (δ) ^b
Pt(C ₆ H ₈)(PPh ₃) ₂ (1)	1721	2.53 (1)	1.76 (1)
Pt(C ₇ H ₁₀)(PPh ₃) ₂ (2)	1781	2.24 (2)	1.69 (3)
Pt(C ₈ H ₁₂)(PPh ₃) ₂ (3)	1793	2.12 (1)	1.60 (2)
Pd(C ₆ H ₈)(PPh ₃) ₂ (4)	1780	2.65 (1)	1.74 (1)
Pd(C ₇ H ₁₀)(PPh ₃) ₂ (5)	1848	2.20 (2)	1.68 (3)
Pt(C ₆ H ₈)(dppe) (6)	1696	2.98 (1)	1.96 (1)
Pt(C ₇ H ₁₀)(dppe) (7)	1761	3.02 (2)	1.97 (3)
Pt(C ₈ H ₁₂)(dppe) (8)	1775	3.05 (1)	1.6–2.1 (2)
Pt(C ₆ H ₈)(<i>t</i> -BuNC)- (PPh ₃) (9)	1705	2.87 (1), 2.56 (1)	1.79 (2)

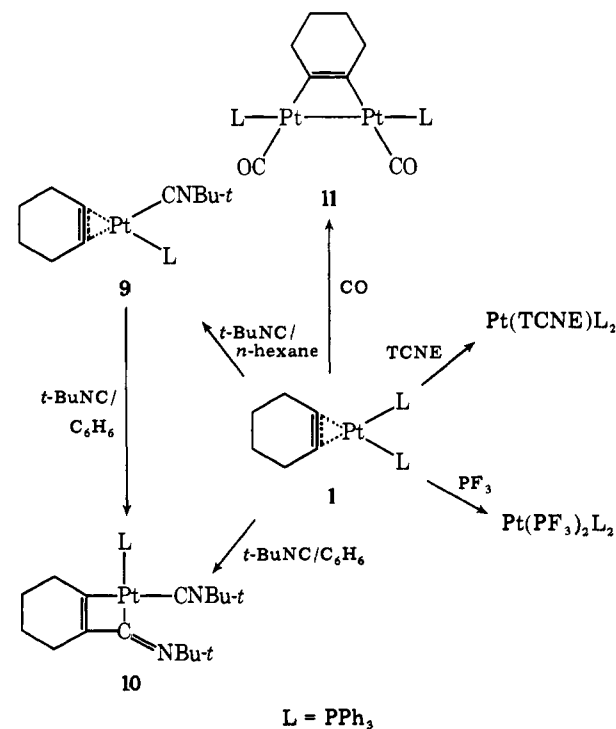
^a Measured in KBr disk. All bands of medium intensity. ^b Parts per million downfield of internal Me₄Si, measured in CDCl₃ at 32 °C. Figures in parentheses denote relative intensities.

cently.^{16–20} We cannot exclude the possibility that the μ -cyclohexyne moiety lies across and above the Pt-Pt bond, as in the well-known Co₂(CO)₆(alkyne) complexes and in the recently prepared Pt₂(PMe₃)₂(PhC₂Ph)(μ -PhC₂Ph),²¹ and attempts to grow single crystals of **11** suitable for x-ray study are being made.

The only reagents which completely displace cyclohexyne from **1** are PF₃ and tetracyanoethylene (TCNE), which give the known complexes Pt(PF₃)₂(PPh₃)₂²² and Pt(TCNE)(PPh₃)₂²³ almost quantitatively. In the case of the PF₃ reaction, attempts to trap the liberated cyclohexyne using 2,5-diphenyl-3,4-benzofuran²⁴ were unsuccessful and, in the absence of the trapping agent, no evidence for cyclotrimers or cyclotetramers of cyclohexyne²⁵ could be obtained. Thus the fate of the C₆H₈ fragment is unknown at present.

The substitution and insertion reactions of **1** discussed so far are summarized in Scheme II.

Scheme II. Substitution and Insertion Reactions of Pt(C₆H₈)(PPh₃)₂



Complexes **1**, **2**, and **6** react with hydrogen chloride or trifluoroacetic acid to give 1-cycloalkenylplatinum(II) complexes PtX(C₆H₉)L₂ [L₂ = 2PPh₃, X = Cl (**12**), CF₃CO₂ (**13**); L₂ = dppe, X = Cl (**14**) and PtX(C₇H₁₁)(PPh₃)₂ [X = Cl (**15**),

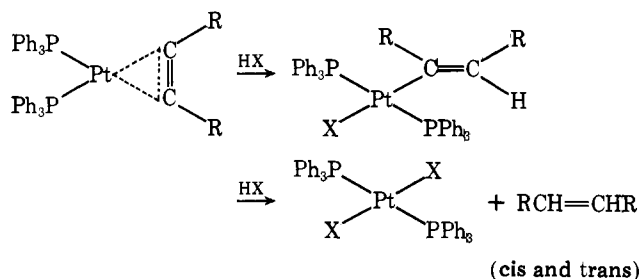
Table II. Selected ^1H NMR and IR Spectroscopic Data for Cycloalkenylbis(triphenylphosphine)platinum(II) Complexes

	^1H NMR ^a			IR, ^b cm^{-1}	
	$\delta(-\text{CH}=\text{C})$	$^3J_{\text{PtH}}$	$\delta(\text{ring CH}_2)$	$\nu(\text{C}=\text{C})$	Other bands
<i>trans</i> -PtCl(C ₆ H ₉)(PPh ₃) ₂ (12)	5.16 (br s)	65	0.34 (2), 1.28 (2), 1.48 (2)	1613	272 [$\nu(\text{PtCl})$]
<i>trans</i> -PtCl(C ₇ H ₁₁)(PPh ₃) ₂ (15)	5.43 (t, $J_{\text{HH}} = 5.6$)	69	0.31 (2), 0.76 (4), 1.42 (2), 1.74 (2)	1600	270 [$\nu(\text{PtCl})$]
<i>trans</i> -Pt(OCOCF ₃)(C ₆ H ₉)- (PPh ₃) ₂ (13)	4.92 (br s)	64	0.46 (2), 0.76 (2), 1.36 (4)	1610	1689, 1405 [$\nu(\text{CO}_2)$], 1189 [$\nu(\text{C}-\text{O})$]
<i>trans</i> -Pt(OCOCF ₃)(C ₇ H ₁₁)- (PPh ₃) ₂ (16)	5.02 (t, $J_{\text{HH}} = 6.0$)	67	0.38 (2), 0.96 (4), 1.2-1.91 (4)	<i>c</i>	1690, 1402 [$\nu(\text{CO}_2)$], 1190 [$\nu(\text{C}-\text{O})$]
<i>cis</i> -Pt(OC ₆ H ₄ CH ₃ - <i>p</i>)(C ₆ H ₉)- (PPh ₃) ₂ (18)	5.30 (d, $^4J_{\text{PH}} = 12$)	44	0.81 (4), 1.42 (2), 1.7-2.3 (2) ^d	1603 ^e	1272 [$\nu(\text{PhO})$]
[Pt(μ -SPh)(C ₆ H ₉)(PPh ₃) ₂] (19)	5.00 (br s)	51	0.60 (4), 1.24 (2), 1.58 (2)	<i>c</i>	
<i>cis</i> -Pt(CH ₂ NO ₂)(C ₆ H ₉)- (PPh ₃) ₂ (26)	5.30 (d, $^4J_{\text{PH}} = 11$)	49	0.78 (2), 1.34 (4), 1.72 (1), 2.38 (1) ^f	1610	1502, 1360 [$\nu(\text{NO}_2)$]
<i>trans</i> -PtH(C ₆ H ₉)(PPh ₃) ₂ (25)	5.42 (br s)	51	1.15 (4), 1.82 (4) ^g	<i>c</i>	1920 [$\nu(\text{PtH})$] ^h

^a Measured in CDCl₃ at 32 °C. Chemical shifts (δ) in parts per million downfield of (CH₃)₄Si. Coupling constants (J) in hertz. All C₆H₉ vinyl resonances showed satellites due to ¹⁹⁵Pt ($I = 1/2$, 34% abundance) (1:4:1 pattern). ^b Measured in KBr disk, except where stated otherwise. All $\nu(\text{C}=\text{C})$ bands were weak, other bands were medium or strong. ^c Not observed, presumably owing to low intensity. ^d $\delta(\text{CH}_3)$ 2.1 (s, 3). ^e Tentative assignment. ^f δ 4.28 (m, 1), 4.72 (m with ¹⁹⁵Pt satellites, 1, PtCH₂); $J_{\text{HH}} = 7$, $^3J_{\text{HP}}(\text{trans}) = 7$, $^3J_{\text{HP}}(\text{cis}) = 4$, $^2J_{\text{PH}} = 84$ Hz). ^g Measured in C₆D₆; $\delta = 4.64$ (t, 1, PtH, $^2J_{\text{HP}}(\text{cis}) = 19.5$, $J_{\text{PH}} = 608$ Hz). ^h In CH₂Cl₂.

CF₃CO₂ (**16**)], which show a characteristic vinyl $\nu(\text{C}=\text{C})$ absorption at 1600-1610 cm^{-1} in their IR spectra (Table II). **1** is also protonated by aqueous HBF₄ to give a stable cyclohexenyl aquo salt, [Pt(C₆H₉)(H₂O)(PPh₃)₂]BF₄ (**17**). The $\nu(\text{PtCl})$ values for **12** and **15** are typical of Cl trans to σ -bonded carbon, while the corresponding value for **14** is somewhat higher, as expected for Cl trans to PR₃. All the cycloalkenyls show a vinyl proton resonance in the usual region δ ca. 5; in the *trans*-triphenylphosphine cyclohexenyl complexes **12** and **13** it is a broad singlet, but in the cycloheptenyl complexes **15** and **16** it is a triplet owing to coupling with the vicinal protons ($^3J_{\text{HH}} = 6$ Hz). In the cyclohexenyl dppe complexes, the vinyl resonance appears as a broad doublet owing to coupling with the *trans* phosphorus atom ($^4J_{\text{PH}} \sim 10$ Hz).

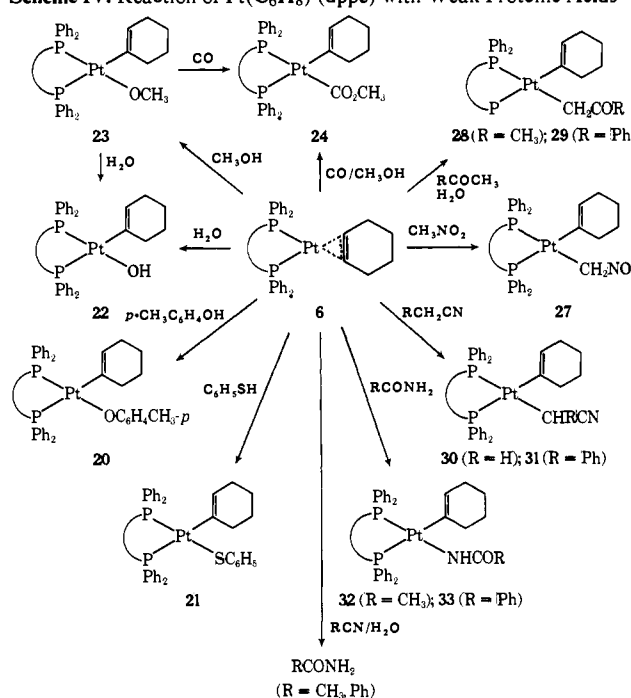
Acyclic acetylene-platinum(0) complexes are similarly protonated by HCl or CF₃CO₂H (Scheme III),^{26,27} though Scheme III. Protonation of Acyclic Alkyne-Platinum(0) Complexes



R = various alkyl or aryl groups; X = Cl, CF₃CO₂

the resulting σ -alkenyl platinum(II) complexes are more readily cleaved by an excess of acid to give the corresponding olefin than are the cycloalkenyls. The *cis* arrangement of hydrogen and platinum on the double bond which has been inferred from the magnitude of $^3J_{\text{PtH}}$ in the acyclic σ alkenyls is, of course, a geometrical necessity in the case of the cycloalkenyls. The magnitude of $^3J_{\text{PtH}}$ in the cycloalkenyls (44-69 Hz) is somewhat less than that in the acyclic alkenyls [$^3J_{\text{PtH}}(\text{cis}) = 63-82$ Hz].²⁷

The cyclohexyne complexes differ markedly from the cycloheptyne complexes in being protonated by relatively weak acids; the dppe derivative **6** is particularly reactive in this respect (Scheme IV). **1** reacts at room temperature with *p*-cresol or thiophenol to give σ -cyclohexenyl complexes, monomeric Pt(OC₆H₄CH₃)(C₆H₉)(PPh₃)₂ (**18**) and dimeric [Pt(SPh)(C₆H₉)(PPh₃)₂] (**19**), respectively; the latter probably contains

Scheme IV. Reaction of Pt(C₆H₈)(dppe) with Weak Protonic Acids

bridging phenylthio groups. **6** reacts similarly to give monomeric complexes Pt(OC₆H₄CH₃)(C₆H₉)(dppe) (**20**) and Pt(SPh)(C₆H₉)(dppe) (**21**), respectively, but the cycloheptyne complex **2** does not react with *p*-cresol under the same conditions. The vinyl resonance of **18** is a broad doublet ($^4J_{\text{PH}} = 12$ Hz), hence the triphenylphosphine ligands are probably mutually *cis*; the same feature is observed in the spectra of the dppe complexes **14**, **20**, and **21**.

More remarkably, the cyclohexyne complexes are also protonated by water and primary alcohols. Thus, on heating **6** with a mixture of water and toluene, the colorless, thermally stable hydroxo complex Pt(OH)(C₆H₉)(dppe) (**22**) can be isolated in good yield. It is soluble in aromatic hydrocarbons, dichloromethane, and chloroform to give air-stable solutions, although in chloroform the chloro complex **14** is formed over a period of hours. The ^1H NMR spectrum of **22** shows the expected doublet vinyl resonance with ¹⁹⁵Pt satellites ($^4J_{\text{PH}} = 10$ Hz, $^3J_{\text{PtH}} = 52$ Hz), but we have been unable to detect a hydroxyl resonance in the range $\delta +10$ to -10 , perhaps be-

Table III. Selected ^1H NMR and IR Spectroscopic Data for $\text{PtX}(\text{C}_6\text{H}_9)(\text{dppe})$

X	^1H NMR ^a					IR, cm^{-1} ^b
	$\delta(\text{=CH-})$	$^4J_{\text{HP}}(\text{trans})$	$^3J_{\text{PtH}}$	δ (others)	J (others)	
Cl, 14	5.21 d	11	<i>c</i>			1604 [$\nu(\text{C}=\text{C})$], 293 [$\nu(\text{PtCl})$]
$\text{OC}_6\text{H}_4\text{CH}_3$ - <i>p</i> , 20	5.13 d	11	49	2.06 s (CH_3) ^d		1602 [$\nu(\text{C}=\text{C})$], 1257 [$\nu(\text{PhO})$]
SPh, 21	5.13 d	12	<i>c</i>			
OH, 22	5.47 d	10	52	<i>e</i>		3692, 3560 [$\nu(\text{OH})$] ^f
OCH_3 , 23	5.35 d ^g	14	51	3.95 d (OCH_3) ^g	5.6 ($^4J_{\text{HP}}(\text{trans})$) 52 ($^3J_{\text{PtH}}$)	1055 [$\nu(\text{C}-\text{O})$]
CO_2CH_3 , 24 ^h	5.13 d	10	74	3.45 s (CO_2CH_3)	7 ($^4J_{\text{PtH}}$)	1640, 1632 [$\nu(\text{C}=\text{O})$] 1030 [$\nu(\text{C}=\text{O})$]
CH_2NO_2 , 27	~ 5.2 ⁱ		<i>c</i>	5.09 dd (PtCH_2)	9.6 ($^3J_{\text{HP}}(\text{trans})$), 5.6 ($^3J_{\text{HP}}(\text{cis})$), 98 ($^2J_{\text{PtH}}$)	1495, 1352 [$\nu(\text{NO}_2)$]
CH_2COCH_3 , 28	5.14 d	10	64	2.78 dd (PtCH_2) 1.84 s (COCH_3)	11 ($^3J_{\text{HP}}(\text{trans})$) 9 ($^3J_{\text{HP}}(\text{cis})$), 106 ($^2J_{\text{PtCH}_2}$)	1620 [$\nu(\text{C}=\text{O})$]
CH_2COPh , 29	4.94 d	9	56	3.26 dd (PtCH_2)	11 ($^2J_{\text{HP}}(\text{trans})$), 8 ($^3J_{\text{HP}}(\text{cis})$), 104 ($^2J_{\text{PtCH}_2}$)	1612 [$\nu(\text{C}=\text{O})$]
CH_2CN , 30	5.25 d	10	67	<i>j</i>		2200 [$\nu(\text{CN})$]
$\text{CH}(\text{CN})\text{Ph}$, 31	5.17 d	9	<i>c</i>	3.95 t (PtCH)	11 ($^3J_{\text{HP}}(\text{trans})$), 11 ($^3J_{\text{HP}}(\text{cis})$), 137 ($^2J_{\text{PtH}}$)	2198 [$\nu(\text{CN})$]

^a Measured in CDCl_3 . CH_2 resonances of C_6H_9 and dppe were broad complex multiplets in range δ 0.6–2.8 in all cases. Protons coupled to ^{195}Pt exhibited a 1:4:1 resonance pattern. ^b Measured in KBr disk, except where stated otherwise. All bands except $\nu(\text{C}=\text{C})$ and $\nu(\text{OH})$ were medium or strong. ^c ^{195}Pt satellites could not be located. ^d Overlaps CH_2 resonances. ^e OH resonance could not be located. ^f Weak bands in CH_2Cl_2 or CHCl_3 . ^g Owing to hydrolysis, peaks due to **22** and to CH_3OH (δ 3.36, s) were also present. ^h Measured in CDCl_3 . ⁱ Broad signal, partly overlaps Pt- CH_2 . ^j Pt- CH_2 overlaps with CH_2 resonances of C_6H_9 and dppe.

cause it is masked by methylene resonances, e.g., $\delta(\text{OH})$ for $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ in CDCl_3 is reported as 1.7.²⁸ However, for other recently prepared hydroxoplatinum(II) complexes it is generally about -2 to -4 .²⁹ The $\nu(\text{OH})$ band in the solid state IR spectrum of **22** cannot be detected, but in chloroform solution there are two strong bands at 3692 and 3560 cm^{-1} . On dilution the intensity of the lower frequency band decreases, which suggests that it arises from an associated, hydrogen-bonded species. The hydroxo-metal formulation is also supported by the observation that **22** catalyzes the hydration of nitriles to amides, a property which is shared by the known hydroxo complexes $\text{M}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Rh}, \text{Ir}$).³⁰ Attempts to isolate a hydroxo complex $\text{Pt}(\text{OH})(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ by reaction of **1** with water/toluene mixture have been unsuccessful.

Methanol reacts with **6** at room temperature to give a σ -methoxoplatinum(II) complex $\text{Pt}(\text{OCH}_3)(\text{C}_6\text{H}_9)(\text{dppe})$ (**23**) in 50% yield as thermally stable, diamagnetic colorless crystals which are soluble in benzene, chloroform, and methanol. The IR spectrum shows a strong band at 1055 cm^{-1} due to $\nu(\text{C}-\text{O})$ and in the ^1H NMR spectrum the methoxyl protons appear as a doublet at δ 3.96 with ^{195}Pt satellites ($^4J_{\text{PH}} = 5.6$ Hz, $^3J_{\text{PtH}} = 51$ Hz). The vinyl proton appears as the expected doublet ($^4J_{\text{PH}} = 10$ Hz). **23** reacts with carbon monoxide under ambient conditions to give the methoxycarbonyl complex $\text{Pt}(\text{CO}_2\text{CH}_3)(\text{C}_6\text{H}_9)(\text{dppe})$ (**24**), which can also be made directly from **6** and methanol in an atmosphere of carbon monoxide. **24** shows typical ester bands in its IR spectrum (Table III), and the ester methyl resonance in the ^1H NMR spectrum is a singlet with ^{195}Pt satellites ($^5J_{\text{PtH}} = 7$ Hz). A benzene solution of **23** also reacts rapidly with water to give the hydroxo complex **22**, but the reverse reaction does not occur when **22** is heated with methanol.

Silver ion promoted hydrolysis of platinum(II)-tertiary phosphine complexes gives unstable products and, until fairly recently, few nonionic hydroxo- or alkoxoplatinum(II) complexes were known. Complexes originally formulated as $\text{Pt}(\text{GePh}_3)(\text{OR})(\text{PET}_3)_2$ [$\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2$]³¹ are now known to be $\text{Pt}(\text{C}_6\text{H}_5)[\text{Ge}(\text{OR})\text{Ph}_2](\text{PET}_3)_2$ following a single-crystal x-ray study of the hydroxo derivative ($\text{R} = \text{H}$).³² Binuclear complexes $\text{Pt}_2(\text{OH})_2(\mu\text{-R}_2\text{EO})_2\text{L}_2$ ($\text{L} =$ various tertiary phosphines; $\text{E} = \text{P}, \text{As}$) containing terminal

hydroxy groups and bridging phosphinato or arsinato groups are also known.³³ Following our initial report,³⁴ a number of planar methoxy complexes of palladium(II) and platinum(II) of general formula $\text{Pt}(\text{OCH}_3)\text{R}(\text{PPh}_3)_2$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, \text{CCl}=\text{CCl}_2, \text{CH}=\text{CCl}_2$) have been made from $\text{PtClR}(\text{PPh}_3)_2$ and sodium methoxide, and the corresponding hydroxo complexes have been obtained by hydrolysis of the methoxides.²⁹ The complexes $\text{Pt}(\text{OH})(\text{CH}_3)(\text{dppe})$ ³⁵ and $\text{Pt}(\text{OCH}_3)(\text{C}_6\text{H}_5)(\text{PET}_3)_2$ ³⁶ have been made by similar routes.

The thermal stability of these alkoxo complexes is surprising because the thermal decomposition of intermediate alkoxides by β -elimination is thought to be responsible for the ready formation of hydrido complexes of the noble metals in basic alcoholic media.³⁷ Thus, although it is unaffected by cold methanol, **1** reacts with methanol under reflux to give a colorless hydrido complex of apparent formula $\text{PtH}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ (**25**) in 69% yield. A similar reaction occurs more slowly in refluxing ethanol, but the yields of **25** and of acetaldehyde are poor (ca. 24%), and **1** is recovered quantitatively from refluxing 2-propanol. Presumably alkoxo complexes similar to **23** are intermediates, but we have been unable to detect them. In contrast, **23** shows no tendency to decompose to a hydrido complex. Reaction of **1** with CH_3OD gives the corresponding 1-deuteriocyclohexenyl complex [$\nu(\text{CD})$ 2198 cm^{-1}], as expected. The ^1H NMR spectrum of **25** in C_6D_6 shows typical cyclohexenyl resonances together with a triplet hydride resonance at δ -4.65 (τ 14.65) ($^2J_{\text{PH}} = 19.5$ Hz, $J_{\text{PtH}} = 608$ Hz), and the IR spectrum of a dichloromethane solution shows a $\nu(\text{PtH})$ band at 1920 cm^{-1} . The spectroscopic parameters, which indicate the hydride ligand to be trans to a ligand of fairly high trans-bond weakening influence, are remarkably similar to those reported by Kudo et al.³⁸ for complexes formulated as *trans*- $\text{PtH}_2(\text{PR}_3)_2$ ($\text{PR}_3 =$ various bulky tertiary phosphines). Recently, such *trans* dihydrides have been prepared by different routes, and characterized unambiguously.^{39–42} Their spectroscopic properties differ from those reported by Kudo et al.,³⁸ and Shaw and Uttley³⁹ have suggested that Kudo's compounds are in fact platinum(IV) hydrides, either $\text{PtH}_4(\text{PR}_3)_2$ or dihydrido complexes containing internal metal-carbon σ bonds. The fact that the IR spectrum of **25** is almost identical with that of **12** in the 1560- and 750- cm^{-1} regions, where ortho-metalated triphenylphosphine

Table IV. Selected ^1H NMR and IR Spectroscopic Data for *N*-Amidoplatinum(II) Complexes

	^1H NMR, δ^a			IR, cm^{-1} b	
	NH	=CH	CH_3	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$
Pt(NHCOCH ₃)(C ₆ H ₉)(dppe) (32)	5.51 br	5.35 d ^c [⁴ <i>J</i> _{HP} (trans) = 10, ³ <i>J</i> _{PtH} = 56]	1.89 s	3390	1615
Pt(NHCOPh)(C ₆ H ₉)(dppe) (33)	6.14 br	5.34 d ^c [⁴ <i>J</i> _{HP} (trans) = 10, ³ <i>J</i> _{PtH} = 52]		3365	1610
<i>trans</i> -Pt(NHCOCH ₃)(C ₆ H ₉)(PPh ₃) ₂ (34)	2.11 br	5.03 br m ^c [³ <i>J</i> _{PtH} = 36]	0.85 s	3370	1608
<i>trans</i> -Pt(NHCOCH ₃)(CH ₃)(PPh ₃) ₂ (35) ^d	3.26 br		1.13 s (COCH ₃); 0.17 t (PtCH ₃) ^c [³ <i>J</i> _{HP} (cis) = 6.5, ² <i>J</i> _{PtH} = 65.5]	3300	1600

^a Measured in CDCl₃, except where stated. ^b Measured in KBr disk. ^c With ¹⁹⁵Pt satellites (1:4:1 pattern). ^d ^1H NMR spectrum measured in C₆D₆.

complexes generally show characteristic absorptions,⁴³ indicates that **25** is probably a platinum(II) hydride PtH(C₆H₉)(PPh₃)₂, not an ortho-metalated platinum(IV) hydride, PtH(C₆H₉)(*o*-C₆H₄PPh₂)₂.⁸¹ However, reaction of **1** with CD₃OD gives the hydride **25** instead of the expected deuteride, presumably as a consequence of exchange with an ortho hydrogen atom of triphenylphosphine.⁴⁴ In contrast with the behavior of the cyclohexyne complexes, the cycloheptyne complex **2** does not react with methanol or 2-methoxyethanol even on prolonged heating or in the presence of KOH.

Nitromethane is a stronger acid than either methanol or ethanol,⁴⁴ and CH₂NO₂⁻ can be expected to have a higher affinity than OCH₃⁻ for the class B ("soft") metal platinum(II). Thus it is not surprising that the cyclohexyne complexes **1** and **6** react with either aqueous or anhydrous nitromethane in refluxing toluene to give air-stable σ -nitromethyl complexes Pt(CH₂NO₂)(C₆H₉)(PPh₃)₂ (**26**) and Pt(CH₂NO₂)(C₆H₉)(dppe) (**27**), respectively. In the ^1H NMR spectrum of **26**, the Pt-CH₂ protons appear as two broad multiplets which, on ³¹P decoupling, sharpen to an AB spectrum with ¹⁹⁵Pt satellites [*J*_{HH} = 7 Hz, ³*J*_{HP}(trans) = 10 Hz, ³*J*_{HP}(cis) = 6 Hz, ²*J*_{PtH} = 98 Hz]. The magnitude of *J*_{Pt-CH₂} shows that the nitromethyl group is σ carbon bonded to the metal, and the inequivalence of the methylene protons indicates that the triphenylphosphine ligands are mutually *cis*; this is confirmed by the cyclohexenyl vinyl proton resonance, which is a broad doublet owing to coupling with the trans phosphorus atom. Nitromethyl-platinum(II) complexes have been postulated as intermediates in the formation of fulminate complexes, e.g., Pt(CNO)₂(PPh₃)₂ from Pt(PPh₃)₄ and nitromethane,⁴⁶ but they have not hitherto been isolated from this reaction.

Neither **1** nor **6** reacts with anhydrous acetone or other methyl ketones on heating but in the presence of water the dppe derivative **6** reacts with acetone or acetophenone to give β -oxoalkylplatinum(II) complexes, Pt(CH₂COR)(C₆H₉)(dppe), as colorless, air-stable, diamagnetic crystals (R = CH₃, **28**; R = Ph, **29**). These show $\nu(\text{C}=\text{O})$ IR bands in the 1600-cm⁻¹ region (Table III). The Pt-CH₂ resonances in their ^1H NMR spectra resemble those of **27**, and the magnitude of *J*_{PtCH₂} (ca. 106 Hz) is strong evidence for the presence of a Pt-C σ bond; this has been confirmed by single-crystal x-ray structural analysis of **29**.³⁴ **1** does not react with methyl ketones even in the presence of water, and **6** does not react with 2-butanone or cyclohexanone. The reactive species in the water-promoted reaction of **6** is undoubtedly the hydroxo complex **23**, since the analogous complexes Pt(OH)(CH₃)(dppe)³⁵ and Pt(OH)(C₆H₅)(PPh₃)₂²⁹ are known to react directly with methyl ketones under mild conditions to give β -oxoalkylplatinum(II) complexes. Closely related β -oxoethyl complexes [PtCl(acac)(CH₂CHO)]⁻ and PtCl(CH₂CHO)(PPh₃)₂ have re-

cently been reported;⁴⁷ the first is the conjugate base of the η^2 -vinyl alcohol complex PtCl(acac)(CH₂=CHOH), while the second is obtained by oxidative addition of chloroacetaldehyde to Pt(PPh₃)₄.

Surprisingly, acetonitrile, which has a larger *pK_a* than acetone,⁴⁸ reacts with **6** under reflux in the absence of water to give the σ -cyanomethylplatinum(II) complex Pt(CH₂CN)(C₆H₉)(dppe) (**30**). In the presence of excess water, however, formation of **30** is suppressed and the main product is acetamide, which is formed catalytically (17 mol per mol of **6** in 3 h).³⁰ The more acidic phenylacetonitrile reacts with **6** even in the presence of water to give the σ -phenylcyanomethyl complex Pt[CH(CN)Ph](C₆H₉)(dppe) (**31**), hydration of the nitrile being almost completely suppressed. The methine proton of **31** appears as a triplet with ¹⁹⁵Pt satellites [³*J*_{HP}(trans), ³*J*_{HP}(cis) ~ 11 Hz, ²*J*_{PtH} = 137 Hz], hence the tertiary carbon atom is attached directly to platinum. σ -Cyanomethylplatinum(II) complexes have been prepared previously by oxidative addition of chloroacetonitrile to platinum(0) complexes.⁴⁹⁻⁵¹

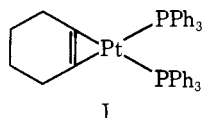
Acetamide and benzamide react with **6** in refluxing toluene to give *N*-amidoplatinum(II) complexes Pt(NHCOR)(C₆H₉)(dppe) (R = CH₃, **32**; R = Ph, **33**). **33** can also be isolated from the reaction of **6** with benzonitrile and water, which gives benzamide catalytically. The triphenylphosphine cyclohexenyl derivative Pt(NHCOCH₃)(C₆H₉)(PPh₃)₂ (**34**) is formed similarly during the hydration of acetonitrile to acetamide catalyzed by **1**. For comparison, we have made Pt(NHCOCH₃)(CH₃)(PPh₃)₂ (**35**) by nucleophilic attack of KOH on the cationic acetonitrile complex [Pt(CH₃)(CH₃CN)(PPh₃)₂]⁺BF₄⁻ (**36**), which is itself readily accessible from Pt(CH₃)(PPh₃)₂ and AgBF₄ in acetonitrile. The fact that **32** and **35** catalyze the formation of acetamide from acetonitrile and water implicates *N*-amido complexes in the catalytic process,³⁰ further investigations of which are in progress. The IR spectra of **32-35** show weak $\nu(\text{NH})$ and intense $\nu(\text{C}=\text{O})$ bands in the 3300- and 1600-cm⁻¹ regions, respectively, and resemble the spectrum of the known *N*-benzamido complex PtCl(NHCOPh)(PEt₃)₂,⁵² which has been isolated from the reaction of phenyl azide with PtHCl(PEt₃)₂. An alternative imino-enol formulation PtN=C(OH)Ph is excluded by the absence of $\nu(\text{OH})$ bands in the 3500-cm⁻¹ region. The ^1H NMR spectra of **32-35** show broad signals due to the NH protons, those of the dppe complexes being 3-4 ppm to lower field than those of the triphenylphosphine complexes. A similar, though less pronounced, trend is evident in the case of the *N*-acetamido methyl resonances (Table IV).

Discussion

The formation of stable small-ring alkyne complexes of

platinum(0), **1** and **2**, demonstrates the utility of the Pt(PPh₃)₂ moiety in trapping short-lived unsaturated hydrocarbons.⁵³ Unfortunately the organic ligands in **1** and **2** are not readily displaced by other unsaturated ligands such as carbon disulfide, so that at present **1** and **2** do not represent convenient sources of the respective cyclic alkynes. The possibility of oxidative displacement of the alkynes remains to be investigated. Although free medium-ring acetylenes and allenes are equilibrated under basic conditions,⁵⁴ there is no evidence for a similar process in their small-ring counterparts owing to their rapid oligomerization. Complexes **1** and **2** can be recovered unchanged from potassium *tert*-butoxide in *tert*-butyl alcohol, and there is therefore no evidence for alkyne → allene isomerization in the complexes. Recently, the preparation of the platinum(0) complexes of 1,2-cycloheptadiene and 1,2-cyclooctadiene, Pt(C₇H₁₀)(PPh₃)₂ and Pt(C₈H₁₂)(PPh₃)₂, has been reported briefly.⁵⁵ Prolonged heating of the 1,2-cycloheptadiene complex with carbon disulfide gives dimers of the cyclic allene, whereas the isomeric cycloheptyne complex is unaffected. The greater stability of the alkyne complex probably reflects the greater strain in cycloheptyne than in 1,2-cycloheptadiene, i.e., more energy is gained in complex formation by relief of strain in the alkyne than in the allene. Another manifestation of relative strain energies is the shift of the base-promoted equilibrium between medium-ring allenes and alkynes toward the former as the ring size decreases.⁵⁴ This is as expected, since in the alkyne four carbon atoms are required to be collinear, whereas in the allene the corresponding number is three.

In trying to account for the chemical differences between the cyclohexyne and cycloheptyne complexes, we start from the structures of **1** and **2** determined by x-ray crystallography.⁹ The coordination geometry and metal-ligand bond lengths of **1** and **2** are similar in most respects to those of Pt(PPh₃)₂ or Pd(PPh₃)₂ complexes of acyclic alkynes.⁵⁶⁻⁶¹ As a consequence of the small ring in **1**, however, the deviation from linearity of the substituents on the coordinated alkyne (the bend-back angle) is 53°, whereas in **2** and all other Pt(PPh₃)₂ complexes of acyclic alkynes the angle is about 40°. Bending is believed to be a consequence of metal → alkyne (π*) back-bonding,⁶²⁻⁶⁴ and the bend-back angle is a rough measure of the perturbation of the alkyne on coordination. The bend-back angles in the free cyclic alkynes have been estimated⁶⁵ as 15° (C₈H₁₂), 25° (C₇H₁₀), and 40° (C₆H₈), although the value found⁶⁶ by electron diffraction in gaseous cyclooctyne is 21° and the C≡C bond length is unexpectedly long (1.23 Å). In forming its Pt(PPh₃)₂ complex, the alkyne substituents of cycloheptyne require to be bent back by only another 15° or so to bring the ligand to the geometry favored for bonding to the metal, and the residual ring strain is accommodated by appreciable distortions of the internal angles at some of the ring methylene carbon atoms from the expected tetrahedral values.⁹ The bend-back angle in free cyclohexyne must be close to the favored value for Pt(alkyne)(PPh₃)₂ complexes, and the fact that a further 13° or so bend-back is observed suggests that there is a very strong σ-π interaction between Pt(PPh₃)₂ and cyclohexyne. The large deviation from linearity calculated for free cyclohexyne will probably lead to an energy difference of ca. 1 eV between the alkyne π orbitals,⁶⁷ so that overlap of the more energetic of these two orbitals with an empty metal orbital is likely to lead to considerable stabilization. The alkyne π orbitals in cyclohexyne could also contain appreciable s character, hence a reasonable representation of **1** may be as a double σ-bonded platinumacyclopene, I. In support of this



idea is the ready substitution of one triphenylphosphine ligand in **1** by *tert*-butyl isocyanide to give **9**, since σ-bonded carbon is known to have a high trans effect.⁶⁸ Moreover, the insertion of *tert*-butyl isocyanide into the platinum-cyclohexyne bond of **9** is, as already noted, reminiscent of the behavior of metal-carbon σ-bonded complexes.

Spectroscopic evidence for the strong platinum-cyclohexyne interaction is provided by the trend in “ν(C≡C)” values in the series Pt(cyclic alkyne)(PPh₃)₂ and Pt(cyclic alkyne)(dppe), viz., C₈H₁₂ > C₇H₁₀ >> C₆H₈ (Table I). The values for the dppe complexes are consistently lower than those of the triphenylphosphine complexes, presumably owing to the greater σ-donor/poorer π-acceptor ability of dppe relative to 2PPh₃. The values for the palladium complexes **4** and **5** are larger than those of their platinum analogues **1** and **2**, as is observed also for acyclic alkyne complexes of these two elements.⁶ Although the values of “ν(C≡C)” are qualitatively consistent with the observation that the coordinated C≡C bond lengths in **1** and **2** are closer to a C=C bond than to a C≡C bond,⁹ the trends in “ν(C≡C)” are not reflected in the C≡C bond lengths, which are identical within experimental error in **1**, **2**, and **3**. Also, the value of “ν(C≡C)” in **9** is lower than that in **1**, which would appear to indicate that *t*-BuNC is a poorer π acceptor than PPh₃, contrary to the conclusion drawn from a comparison of ν(CO) values in Ni(CO)₂(*t*-BuNC)₂ and Ni(CO)₂(PPh₃)₂.⁶⁹ It is noteworthy that, in the series M(RC₂R)L₂, when M = Ni and R = Ph, the “ν(C≡C)” values are in the expected order L = *t*-BuNC > PPh₃, whereas for M = Pd and R = CO₂CH₃ the order is reversed.^{6,70} These observations emphasize the dangers of drawing conclusions from simple comparison of “ν(C≡C)” values of coordinated alkynes; they may be vitiated by vibrational coupling between ν(C≡C) and other modes such as ν(C=O) and δ(CH₂).

Despite their stability, cyclohexyne-platinum(0) complexes are very reactive, much more so than their cycloheptyne analogues. The reactions of **1** with CO and *t*-BuNC, and the ease with which **1** and **6** are protonated by water, methanol, and other weak acids, indicate that cyclohexyne bound to one metal atom is severely strained, even when the metal is in a low oxidation state. Protonation probably occurs by initial oxidative addition at the metal atom and subsequent transfer of hydrogen to the ring, as suggested also for the protonation of acyclic alkyne-platinum(0) complexes by strong acids.^{26,27} An oxidative addition intermediate has been isolated from the reaction of **1** with methyl iodide.⁷¹

The reaction of **1** and **6** with carbon acids gives a series of functionalized alkylplatinum(II) complexes which are not readily accessible by other routes and which should prove useful in studying oxidative addition/reductive elimination sequences in platinum(II) chemistry. Nitromethane, acetonitrile, or phenylacetonitrile react with **6** under anhydrous conditions, presumably by an oxidative addition/hydrogen transfer mechanism, whereas methyl ketones react only in the presence of water via the preformed hydroxo complex **22**. A related oxidative addition of acetonitrile, acetone, and other carbon acids to the fragments M(dmpe)₂ [M = Fe, Ru; dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂] formed by elimination of naphthalene from MH(C₁₀H₇)(dmpe)₂ has recently been reported.⁷²

Experimental Section

IR spectra were measured on a Perkin-Elmer 457 instrument calibrated with polystyrene; ¹H NMR spectra were recorded on a Varian HA-100 instrument using tetramethylsilane as internal reference. Melting points were measured in open capillaries on a Gallenkamp hot-stage apparatus and are uncorrected. Mass spectra of Pt(C₆H₈)(PPh₃)₂ and Pt(C₇H₁₀)(PPh₃)₂ were measured by Mr. K. Goggin on an AEI-MS9 instrument at 70 eV. Analyses and osmometric molecular weights (Model 301A, Mechrolab, chloroform, 37 °C)

Table V. Melting Points, Elemental Analysis, and Molecular Weight Data for Cyclic Alkyne Metal Complexes and Derivatives

Complex	Mp, °C	% C		% H		% P		Mol wt	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Pt(C ₆ H ₈)(PPh ₃) ₂ (1)	157-159	63.1	63.3	4.8	5.0	7.75	7.8	799	729 ^a
Pt(C ₇ H ₁₀)(PPh ₃) ₂ (2)	163-166	63.45	63.6	5.0	5.0	7.6	7.5	813	820 ^b
Pd(C ₆ H ₈)(PPh ₃) ₂ (4)	89-92	70.9	70.9	5.4	5.4	8.7	8.5		
Pd(C ₇ H ₁₀)(PPh ₃) ₂ (5)	100-102	71.2	71.25	5.6	5.5	8.55	8.2		
Pt(C ₆ H ₈)(dppe) (6)	163-166	57.2	57.2	4.8	4.7	9.2	9.2	676	644
Pt(C ₇ H ₁₀)(dppe) (7)	172-174	57.6	57.6	5.0	5.1	9.0	9.0	688	631
Pt(C ₈ H ₁₂)(dppe) (8)	177-178	58.2	57.7	5.2	5.8	8.8	8.4		
Pt(C ₆ H ₈)(PPh ₃)(<i>t</i> -BuNC) (9)	105-108	56.1	56.1	5.2	5.1	5.0	5.0	620	637
Pt(C ₆ H ₈)(PPh ₃)(<i>t</i> -BuNC) ₂ C ₆ H ₆ (10)	113-114	61.4	61.3	6.1	6.6	4.0	3.8		
Pt ₂ (C ₆ H ₈)(CO) ₂ (PPh ₃) ₂ C ₆ H ₆ (11)	100	53.2	53.5	3.9	4.1	5.5	5.6	1187	1057 ^c
PtCl(C ₆ H ₉)(PPh ₃) ₂ (12)	205-207	60.3	60.2	4.7	4.8	7.4	7.3 ^d	836	769
Pt(O ₂ CCF ₃)(C ₆ H ₉)(PPh ₃) ₂ (13)	190	57.8	58.2	4.3	4.5	6.8	6.9	829	914
PtCl(C ₆ H ₉)(dppe)-CHCl ₃ (14)	217-218	47.8	47.1	4.1	4.4	6.5	7.0 ^e	710	790
PtCl(C ₇ H ₁₁)(PPh ₃) ₂ (15)	194-198	60.7	60.4	4.9	4.6	7.3	7.05 ^f		
Pt(O ₂ CCF ₃)(C ₇ H ₁₁)(PPh ₃) ₂ (16)	178-179	58.25	58.5	4.45	4.4	6.7	6.8	929	819
[Pt(C ₆ H ₉)(H ₂ O)(PPh ₃) ₂]BF ₄ -CHCl ₃ (17)	130-133	50.4	50.7	4.1	4.4	6.05	5.8 ^g		
Pt(OC ₆ H ₄ CH ₃)(C ₆ H ₉)(PPh ₃) ₂ (18)	150-152	64.8	63.8	5.1	5.3	6.8	7.7		
[Pt(SPh)(C ₆ H ₉)(PPh ₃) ₂] (19)	206-208	55.6	55.1	4.5	4.8	4.8	4.8	1201	1290
Pt(OC ₆ H ₄ CH ₃)(C ₆ H ₉)(dppe) (20)	182-183	59.9	60.2	5.2	5.45	7.9	7.55	783	759
Pt(SPh)(C ₆ H ₉)(dppe) (21)	234-236	56.9	56.9	5.0	5.1	8.2	7.6		
Pt(OH)(C ₆ H ₉)(dppe) (22)	178-181	55.6	55.9	4.95	4.9	9.0	8.2	692	691
Pt(OCH ₃)(C ₆ H ₉)(dppe) (23)	160	56.2	56.1	5.1	5.65	8.8	8.55		
Pt(CO ₂ CH ₃)(C ₆ H ₉)(dppe) (24)	163-165	55.5	55.0	4.9	5.1	8.45	8.3	734	759
PtH(C ₆ H ₉)(PPh ₃) ₂ (25)	143-148	62.9	62.5	5.0	4.9	7.7	7.4	802	860
Pt(CH ₂ NO ₂)(C ₆ H ₉)(PPh ₃) ₂ (26)	145-151	60.0	59.8	4.8	5.0	7.2	6.8 ^h	860	864
Pt(CH ₂ NO ₂)(C ₆ H ₉)(dppe)·0.5C ₂ H ₅ OH (27)	176-178	53.9	54.4	5.1	4.8	8.2	8.2 ⁱ		
Pt(CH ₂ COCH ₃)(C ₆ H ₉)(dppe) (28)	182-184	57.4	57.35	5.2	5.3	8.5	8.2	732	707
Pt(CH ₂ COPh)(C ₆ H ₉)(dppe)·C ₂ H ₅ OH (29) ^j	166-168	60.1	60.3	5.5	5.7	7.4	7.2		
Pt(CH ₂ CN)(C ₆ H ₉)(dppe) (30)	136-144	57.1	57.1	4.9	5.2	8.7	8.4		
Pt[CH(CN)Ph](C ₆ H ₉)(dppe)·CH ₂ Cl ₂ (21)	190-193	56.2	56.6	4.9	4.7	7.1	6.9 ^k		
Pt(NHCOCH ₃)(C ₆ H ₉)(dppe) (32)	197-201	55.7	55.65	5.1	5.2	8.5	8.2 ^l		
Pt(NHCOPh)(C ₆ H ₉)(dppe) (33)	192-195	58.9	58.0	4.95	5.4	7.8	7.6 ^m	795	762
Pt(NHCOCH ₃)(C ₆ H ₉)(PPh ₃) ₂ (34)	149-150	61.5	61.7	5.05	5.25	7.2	6.9 ⁿ		

^a 799 (mass spectrometry). ^b 813 (mass spectrometry). ^c By osmometry in C₆H₆. ^d % Cl: calcd, 4.9; found, 4.2. ^e % Cl: calcd, 17.1; found, 17.1. ^f % Cl: calcd, 4.2; found, 4.5. ^g % Cl: calcd, 10.4; found, 9.9. ^h % N: calcd, 1.6; found, 1.5. ⁱ % N: calcd, 1.9; found, 2.0. Presence of 0.5 mol of C₂H₅OH confirmed by ¹H NMR in CDCl₃. ^j Presence of 1 mol of C₂H₅OH confirmed by ¹H NMR in CDCl₃ and by x-ray study (ref 34). ^k % N: calcd, 1.6; found, 1.6. Presence of 1 mol of CH₂Cl₂ confirmed by ¹H NMR in CDCl₃. ^l % N: calcd, 1.9; found, 2.0. ^m % N: calcd, 1.8; found, 1.8. ⁿ % N: calcd, 1.6; found, 1.5.

were carried out by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). Spectroscopic data are in Tables I-IV; analytical data are in Table V.

Solvents were routinely dried and degassed by standard techniques before use, and all preparations were carried out under nitrogen, although most of the platinum complexes were air stable once isolated from solution.

Preparations. Bis(triphenylphosphine)cyclohexyneplatinum(0), Pt(C₆H₈)(PPh₃)₂ (1). To a magnetically stirred suspension of 1% sodium amalgam prepared from freshly cut sodium (0.31 g) and mercury (30 g) in freshly distilled tetrahydrofuran (30 mL) was added Pt(PPh₃)₃⁷³ (2.2 g, 2.24 mmol). After 5 min a solution of 1,2-dibromocyclohexene⁷⁴ (1.61 g, 6.72 mmol) in tetrahydrofuran (15 mL) was added and the mixture was stirred for 4 h at room temperature. Excess of amalgam was separated either by filtration or centrifugation and the supernatant liquid was evaporated in vacuo to give a deep brown oily residue which crystallized on trituration with a few milliliters of ethanol. Recrystallization from benzene/ethanol gave colorless crystals of **1** (1.06 g, 59%).

Bis(triphenylphosphine)cycloheptyneplatinum(0), Pt(C₇H₁₀)(PPh₃)₂ (2). (1) The procedure for **1** was followed using 1,2-dibromocycloheptene⁷⁵ instead of 1,2-dibromocyclohexene. Recrystallization from benzene/ethanol gave colorless crystals of **2** in 81% yield.

(2) A mixture of Pt(PPh₃)₃ (0.196 g, 0.2 mmol), 1,2-cycloheptanedione bis(hydrazone) (0.14 g, 1 mmol),⁷⁶ mercuric oxide (0.54 g, 2.5 mmol), sodium sulfate (5 g), and benzene (10 mL) was heated at 45-50 °C for 1.5 h. When gas evolution had ceased the mixture was filtered and the dark brown filtrate was evaporated in vacuo to give

a brown, viscous oil. Addition of ethanol gave colorless crystals of **2** (0.04 g, 25%).

Bis(triphenylphosphine)cyclooctyneplatinum(0), Pt(C₈H₁₂)(PPh₃)₂ (3). This was prepared as under (2) above using 1,2-cyclooctanedione bis(hydrazone)⁷⁷ in place of its cycloheptanedione analogue. The crude product was recrystallized from benzene/ethanol to give colorless crystals of **3** in 20% yield, mp 180-182 °C dec (lit.^{8a,8b} 180-182, 205-207 °C dec).

Attempted Preparation of Bis(triphenylphosphine)cyclopentynepalladium(0), Pd(C₅H₆)(PPh₃)₂. A mixture of Pd(PPh₃)₃ (0.39 g, 0.42 mmol) and excess of 1% sodium amalgam in tetrahydrofuran (20 mL) was treated with 1,2-dibromocyclopentene⁷⁸ (0.45 g, 2 mmol) and the mixture was stirred for 3.5 h at room temperature. Since no color change was observed, the mixture was heated under reflux for 48 h. Evaporation in vacuo of the filtered solution gave unreacted Pd(PPh₃)₃ and 1,2-dibromocyclopentene.

Bis(triphenylphosphine)cyclohexynepalladium(0), Pd(C₆H₈)(PPh₃)₂ (4). To a stirred suspension of 1% sodium amalgam prepared from sodium (0.1 g) and mercury (10 g) in freshly distilled tetrahydrofuran (15 mL) were added successively Pd(PPh₃)₄⁷⁹ (0.41 g, 0.4 mmol) and 1,2-dibromocyclohexene (0.29 g, 1.2 mmol). The mixture was stirred for 1-1.5 h at room temperature and filtered or centrifuged, and the yellow liquid was evaporated in vacuo to give an oily residue. Addition of a few milliliters of degassed *n*-hexane gave an off-white solid which, on recrystallization from either toluene/*n*-hexane or ether, gave colorless crystals of **4** (0.083 g, 30%).

Lower yields and less pure product result if the reaction mixture is stirred for more than 2 h.

Bis(triphenylphosphine)cycloheptynepalladium(0), Pd(C₇H₁₀)(PPh₃)₂ (5). The procedure for **4** was followed using 1,2-dibromocycloheptene

in place of 1,2-dibromocyclohexene. Recrystallization from benzene/*n*-hexane gave colorless crystals of **5** in 25% yield.

1,2-Bis(diphenylphosphino)ethanecyclohexyneplatinum(0), Pt(C₆H₅)₂(dppe) (6**).** A mixture of **1** (0.079 g, 0.1 mmol), dppe (0.043 g, 0.11 mmol), and benzene (5 mL) was heated under reflux for 3 h. The solution was evaporated in vacuo and the residue was washed with *n*-hexane. The hexane-insoluble solid was recrystallized from benzene/*n*-hexane to give colorless crystals of **6** quantitatively. Evaporation of the *n*-hexane washings gave triphenylphosphine (0.05 g, 95%).

1,2-Bis(diphenylphosphino)ethanecycloheptyneplatinum(0), Pt(C₇H₁₀)(dppe) (7**), and -cyclooctyneplatinum(0), Pt(C₈H₁₂)(dppe) (**8**).** These were prepared similarly to **6** starting from **2** and **3**, respectively. After recrystallization from benzene/ethanol the colorless, crystalline products were obtained in 60 and 75% yields, respectively.

Attempted Reaction of 1 with 2,2'-Bipyridyl. A mixture of **1** (0.080 g, 0.1 mmol), 2,2'-bipyridyl (0.019 g, 0.12 mmol), and benzene (5 mL) was heated under reflux for 45 h. The solution was evaporated in vacuo and the residue, on recrystallization from benzene/*n*-hexane, gave **1** quantitatively.

Cyclohexyne-*tert*-butyl isocyanide(triphenylphosphine)platinum(0), Pt(C₆H₈)(PPh₃)(*t*-BuNC) (9**).** *tert*-Butyl isocyanide (0.022 g, 0.27 mmol) was added to a suspension of **1** (0.11 g, 0.14 mmol) in *n*-hexane (5 mL) and the mixture was stirred at ambient temperature for 1 h. The colorless, crystalline product which separated was filtered off, washed with *n*-hexane, and dried in vacuo to give analytically pure **9** quantitatively.

3,4,5,6-Tetrahydro-1-[(*tert*-butyl isocyanide)(triphenylphosphine)]platina-2-*tert*-butyliminocyclobutacyclohexene, (*t*-BuNC)(Ph₃P)Pt[(C=N*Bu-t*)(C₆H₈)] (10**).** A mixture of **1** (0.08 g, 0.1 mmol), *tert*-butyl isocyanide (0.022 g, 0.26 mmol), and benzene (5 mL) was stirred at room temperature for 10 h. Solvent was evaporated in vacuo to give a yellow, oily residue which crystallized on addition of *n*-hexane. Recrystallization from benzene/*n*-hexane gave **10** as a pale yellow, crystalline solid (0.047 g, 67%).

10 was also isolated in 70% yield from reaction of **9** with *t*-BuNC in benzene: IR (KBr) 1570, 1601 cm⁻¹ m [ν(C=C), ν(C=N)]; ¹H NMR (CDCl₃) δ 0.79 (s, 9, *t*-Bu), 1.74 (s, 9, *t*-Bu), 1.2–1.9 (m, 6, CH₂), 2.84 (m, 2, CH₂).

Attempted Reaction of 2 with *tert*-Butyl Isocyanide. This was carried out as described for the synthesis of **9**. The cycloheptyne complex **2** was recovered unchanged after stirring at room temperature for 20 h.

Bis(triphenylphosphine)- μ -cyclohexyne-dicarbonyldiplatinum(Pt-Pt), Pt₂(C₆H₈)(CO)₂(PPh₃)₂ (11**).** Carbon monoxide was bubbled into a refluxing solution of **1** (0.16 g, 0.2 mmol) in benzene (15 mL) for 3 h. The yellow-brown solution was concentrated under reduced pressure to 2 mL and the product was precipitated by addition of *n*-heptane (5 mL). Yellow, crystalline **11** was obtained by recrystallization from benzene/*n*-heptane under CO: yield 0.078 g (66%); IR (CH₂Cl₂) 2035 vs., 1992 cm⁻¹ m [ν(CO)]; NMR (CDCl₃) δ 2.55 (m with ¹⁹⁵Pt satellites, 1, α -CH₂, ³J_{PtH} = 34 Hz), 1.80 (m, 1, β -CH₂).

2 was recovered unchanged after a similar treatment with CO for 6.5 h.

Reaction of 1 with PF₃. PF₃ was bubbled into a refluxing solution of **1** (0.24 g, 0.3 mmol) and 2,5-diphenyl-3,4-benzofuran (0.084 g, 0.3 mmol) in benzene for 2 h. The yellow solution was evaporated to dryness under reduced pressure to give a yellow solid which was washed with carbon tetrachloride. The residue when recrystallized from benzene/*n*-heptane gave Pt(PF₃)₂(PPh₃)₂ quantitatively, mp 200 °C dec (lit.²² 202 °C dec). The CCl₄ extract was chromatographed on alumina. Elution with CCl₄ gave 2,5-diphenyl-3,4-benzofuran (0.02 g). Elution with methanol and subsequent evaporation of the colorless eluate gave unidentified colorless crystals (0.05 g) which showed a strong ν(C=O) band at 1664 cm⁻¹ (KBr disk) but no ν(CH₂) bands.

Reaction of 1 with Tetracyanoethylene (TCNE). A suspension of **1** (0.08 g, 0.1 mmol) in *n*-hexane (10 mL) was treated with a solution of TCNE (0.014 g, 0.11 mmol) in benzene (3 mL). The yellow, crystalline product which precipitated almost immediately was identified as Pt(PPh₃)₂(TCNE) from its IR spectrum.²³

2 behaved similarly on reaction with TCNE.

Attempted Reaction of 1 with Carbon Disulfide. A solution of **1** (0.08 g, 0.1 mmol) in carbon disulfide (5 mL) was heated under reflux for 30 min. **1** was recovered unchanged when solvent was removed in

vacuo. **2** also failed to react with CS₂ under reflux over a 3-h period, even in the presence of 2,5-diphenyl-3,4-benzofuran. Prolonged refluxing caused decomposition.

Attempted Reaction of 1 with Alkynes. A solution containing **1** (0.04 g, 0.05 mmol) and dimethyl acetylenedicarboxylate (0.015 g, 0.1 mmol) in chloroform (5 mL) was stirred for 3 h at room temperature. The oily residue obtained after removal of solvent crystallized on addition of ethanol and unchanged **1** was recovered quantitatively. Diphenylacetylene and methyl propiolate likewise did not react with **1**.

Attempted Isomerization of Coordinated Cyclohexyne to 1,2-Cyclohexadiene. A mixture of **1** (0.080 g, 0.1 mmol), potassium *tert*-butoxide (0.028 g, 0.25 mmol), *tert*-butyl alcohol (2 mL), and toluene (5 mL) was heated under reflux for 16 h. Solvents were removed under reduced pressure and the residue was extracted with benzene. Evaporation of the benzene solution gave unchanged **1** quantitatively.

Reactions of Cyclic Alkyne Complexes with Protonic Acids. (1) Hydrogen Chloride. (a) Benzene saturated with HCl (0.22 mL, 0.1 mmol) was added to a solution of **1** (0.08 g, 0.1 mmol) and the mixture was stirred for 20 min at room temperature. Evaporation under reduced pressure gave an amorphous solid which, on recrystallization from dichloromethane/ether, gave colorless, crystalline *trans*-PtCl(C₆H₉)(PPh₃)₂ (**12**, 0.062 g, 74%).

(b) Similarly prepared from **2** and **6**, respectively, were *trans*-PtCl(C₇H₁₁)(PPh₃)₂ (**15**) (47% yield after recrystallization) and PtCl(C₆H₉)(dppe)·CHCl₃ (**14**) (90% yield after recrystallization from chloroform/ether).

(2) Trifluoroacetic Acid. (a) To a solution of **1** (0.08 g, 0.1 mmol) in benzene (10 mL) was added CF₃CO₂H (0.013 g, 0.11 mmol). The mixture was stirred at room temperature for 1 h at room temperature and solvent was then evaporated in vacuo. The colorless crystals which separated were recrystallized from benzene/*n*-hexane to give *trans*-Pt(O₂CCF₃)(C₆H₉)(PPh₃)₂ (**13**, 0.075 g, 80%).

(b) Similarly prepared from **2** was *trans*-Pt(O₂CCF₃)(C₇H₁₁)(PPh₃)₂ (**16**) in 64% yield.

(3) Fluoroboric Acid. A suspension of **1** (0.08 g, 0.1 mmol) in 40% aqueous HBF₄ (3 mL) was heated at 50–60 °C for 2 h. The colorless powder which separated was filtered off and washed successively with water and benzene. Recrystallization from a large volume of hot chloroform gave the colorless, crystalline aquo salt [Pt(C₆H₉)(H₂O)(PPh₃)₂]BF₄·CHCl₃ (**17**, 0.07 g, 78%). Its very low solubility even in polar solvents such as nitrobenzene, dimethyl sulfoxide, nitromethane, and chloroform prevented measurement of the ¹H NMR spectrum.

(4) *p*-Cresol. (a) A mixture of **1** (0.08 g, 0.1 mmol), *p*-cresol (0.012 g, 0.11 mmol), and benzene (5 mL) was stirred for 2.5 h at room temperature. Removal of solvent under reduced pressure gave a pale yellow oil which crystallized on addition of *n*-hexane. Recrystallization from benzene/*n*-hexane gave colorless, crystalline *cis*-Pt(OC₆H₄CH₃-*p*)(C₆H₉)(PPh₃)₂ (**18**, 0.068 g, 75%).

2 was recovered unchanged on attempted reaction with *p*-cresol.

(b) Reaction of **6** with *p*-cresol as described above gave Pt(OC₆H₄CH₃-*p*)(C₆H₉)(dppe) (**20**) in 65% yield.

(5) Thiophenol. (a) A mixture of **1** (0.08 g, 0.1 mmol), thiophenol (0.013 g, 0.13 mmol), and benzene (5 mL) was stirred for 1 h at room temperature. Removal of solvent under reduced pressure gave a solid which, on recrystallization from benzene/ethanol, gave pale yellow crystals of [Pt(SPh)(C₆H₉)(PPh₃)₂] (**19**, 0.056 g, 86%).

(b) Similarly prepared from **6** was Pt(SPh)(C₆H₉)(dppe) (**21**) in 57% yield after recrystallization from chloroform/*n*-hexane.

(6) Water. (a) A mixture of **6** (0.067 g, 0.1 mmol), water (1 mL), and toluene (5 mL) was heated under reflux for 17 h. Concentration of the pale yellow solution gave a yellow solid which, on recrystallization from benzene/*n*-heptane, gave colorless, crystalline Pt(OH)-(C₆H₉)(dppe) (**22**, 0.044 g, 65%).

(b)⁸⁰ A solution of **6** (0.63 g, 0.95 mmol) in benzene (40 mL) was treated with methanol (20 mL) to give a yellow solution and then after 1 min with water (1 mL). After being allowed to stand at room temperature for 45 min the solution was evaporated to dryness under reduced pressure. The residue afforded 0.56 g (86%) of **22** after recrystallization from benzene/*n*-heptane.

(7) Alcohols. (a) A mixture of **1** (0.08 g, 0.1 mmol), benzene (5 mL), and methanol (5 mL) was heated under reflux for 1.5 h. Removal of solvent under reduced pressure gave a yellow solid which showed ν(PtH) bands at 1855 and 1940 cm⁻¹ (br) in the IR spectrum. Recrystallization from benzene/methanol gave colorless, crystalline

trans-PtH(C₆H₉)(PPh₃)₂ (**25**, 0.055 g, 69%) which appears to exist in two different crystalline forms having ν (PtH) bands at 1855 and 1940 cm⁻¹. Either one or both forms may be obtained on recrystallization; their solution IR and ¹H NMR spectroscopic properties are identical (Table II).

Reaction of **1** with CH₃OD or CD₃OD gave colorless, crystalline *trans*-PtH(C₆H₈D)(PPh₃)₂, mp 136–142 °C dec, in 62% yield: IR (KBr) 1855, 1950 [ν (PtH)], 2198 cm⁻¹ [ν (CD)].

(b) **1** (0.16 g, 0.2 mmol) was heated under reflux in benzene/ethanol (20 mL) for 16 h. Evolved acetaldehyde was trapped as its 2,4-dinitrophenylhydrazone (0.013 g, 29%), and workup as above gave **25** (0.038 g, 24%).

Under similar conditions **1** did not react with 2-propanol.

(c) A colorless solution of **6** (0.067 g, 0.1 mmol) in benzene (3 mL) immediately turned yellow on addition of absolute methanol (2 mL). After 1 h at room temperature, the solution was evaporated in vacuo to ca. 1 mL and refrigerated. The colorless crystals which separated were filtered and washed with absolute methanol at –30 °C. After drying in vacuo the yield of Pt(OCH₃)(C₆H₉)(dppe) (**23**) was 0.04 g (57%). Refluxing the reaction solution for 1 h gave only **23** and no hydride was detected. Reaction with water gave **22** in good yield (see above).

(d) Carbon monoxide was passed into a solution of **6** (0.067 g, 0.1 mmol) in benzene (5 mL) and methanol (5 mL) at room temperature for 1 h. Removal of solvents in vacuo gave a viscous yellow oil which crystallized on trituration with methanol. Recrystallization from benzene/*n*-hexane gave colorless, crystalline Pt(CO₂CH₃)(C₆H₉)(dppe) (**24**, 0.045 g, 61%).

24 was also obtained in 70% yield by carbonylation of the isolated methoxo complex **24** in methanol.

(8) **Nitromethane**. (a) A solution of **1** (0.08 g, 0.1 mmol) in toluene (5 mL) and nitromethane (0.91 g, 15 mmol) was heated under reflux for 5 h. The dark yellow solid which remained after solvents had been removed under reduced pressure was recrystallized from benzene/*n*-hexane to give colorless, crystalline *cis*-Pt(CH₂NO₂)(C₆H₉)(PPh₃)₂ (**26**, 0.047 g, 54%).

(b) Similarly prepared from **6** and nitromethane, and recrystallized from benzene/ethanol, was Pt(CH₂NO₂)(C₆H₉)(dppe)·0.5C₂H₅OH (**27**, 0.03 g, 38%).

(9) **Methyl Ketones**. (a) A mixture of **6** (0.067 g, 0.1 mmol), acetophenone (0.036 g, 0.3 mmol), water (2 mL), and toluene (5 mL) was heated under reflux for 5 h. Solvent was removed in vacuo to give a brown oil which crystallized on addition of a few milliliters of ethanol/*n*-heptane. Recrystallization from benzene/ethanol gave colorless, crystalline Pt(CH₂COPh)(C₆H₉)(dppe)·C₂H₅OH (**29**, 0.03 g, 37%). In the absence of water, **6** was recovered unchanged.

1 failed to react with aqueous acetophenone under the same conditions.

(b) A mixture of **6** (0.067 g, 0.1 mmol), acetone (5 mL), and water (0.5 mL) was heated under reflux for 5 h. Workup as in (a) and recrystallization from benzene/*n*-hexane gave colorless, crystalline Pt(CH₂COCH₃)(C₆H₉)(dppe) (**28**, 0.06 g, 84%).

(10) **Nitriles**. (a) A mixture of **6** (0.067 g, 0.1 mmol), acetonitrile (5 mL), and water (2 mL) was heated under reflux for 3 h. Concentration of the mixture under reduced pressure gave a colorless solid which, on sublimation at 80 °C (bath) (5 mmHg), gave acetamide (0.105 g, 17 mol/mol **6**), mp 78–81 °C. The yellow, involatile residue was recrystallized from dichloromethane/ether to give colorless crystals, mp 158–160 °C dec, tentatively identified as Pt(NHCOCH₃)₂(dppe), yield 0.04 g (72%). Anal. Calcd for C₃₀H₃₂N₂O₂P₂Pt: C, 50.77; H, 4.55; N, 3.95. Found: C, 50.56; H, 4.74; N, 4.80.

(b)⁸⁰ A solution of **6** (0.12 g, 0.18 mmol) in acetonitrile (5 mL) which had been freshly distilled from P₄O₁₀ was heated under reflux for 24 h. Solvent was removed in vacuo and the residue was recrystallized from dichloromethane/*n*-hexane to give colorless Pt(CH₂CN)(C₆H₉)(dppe) (**30**, 0.083 g, 67%).

(c) A mixture of **1** (0.16 g, 0.2 mmol), acetonitrile (10 mL), water (3 mL), and benzene (3 mL) was heated under reflux for 16 h (no reaction was evident after 3 h, **1** being recovered quantitatively). The residue, after removal of solvents, afforded acetamide (0.81 g, 58 mol/mol **1**) on sublimation. The involatile residue on recrystallization from benzene/*n*-hexane gave *trans*-Pt(NHCOCH₃)(C₆H₉)(PPh₃)₂ (**34**, 0.07 g, 40%).

(d) A mixture of **6** (0.067 g, 0.1 mmol), phenylacetonitrile (2 mL), water (2 mL), and toluene (5 mL) was heated at 90–100 °C for 8 h. Evaporation in vacuo gave a yellow oil which crystallized on addition

of ether. Recrystallization from dichloromethane/*n*-hexane gave colorless, crystalline Pt[CH(CN)Ph](C₆H₉)(dppe) (**31**, 0.046 g, 53%).

(11) **Amides**. (a) A mixture of **6** (0.067 g, 0.1 mmol), acetamide (0.018 g, 0.3 mmol), and toluene (6 mL) was heated under reflux for 5 h. Solvent was removed under reduced pressure to give a yellow oil which crystallized on addition of *n*-heptane. Recrystallization from benzene/*n*-heptane gave colorless, crystalline Pt(NHCOCH₃)(C₆H₉)(dppe) (**32**, 0.052 g, 70%).

(b) A similar reaction between **6** and benzamide gave colorless, crystalline Pt(NHCOPh)(C₆H₉)(dppe) (**33**, 0.041 g, 50%).

Acetonitrilebis(triphenylphosphine)methylplatinum(II) Tetrafluoroborate Benzene Solvate, [Pt(CH₃)(CH₂CN)(PPh₃)₂]BF₄·C₆H₆ (**36**). A suspension of *trans*-PtI(CH₃)(PPh₃)₂ (0.28 g, 0.33 mmol) in acetonitrile (5 mL) was treated with a solution of silver tetrafluoroborate (0.065 g, 0.33 mmol) in acetonitrile (1 mL) to give an immediate precipitate of silver iodide. After 10 min at room temperature the solution was filtered and concentrated under reduced pressure to give an oil which crystallized on addition of ether. Recrystallization from benzene/acetonitrile gave colorless crystals of **36** (0.22 g, 80%): mp 188–190 °C dec; ¹H NMR (CD₂Cl₂, CH₂Cl₂ internal reference) 0.08 (t with ¹⁹⁵Pt satellites, 3, ³J_{H-P} = 7.2, ²J_{Pt-H} = 78 Hz, PtCH₃), 1.22 (s, 3, ⁴J_{Pt-H} = 7 Hz, CH₃CN), 7.3–7.8 (m, 30, Ph + C₆H₆); IR (KBr) 1060 [ν (BF)], ν (CN) not observed. Anal. Calcd for C₄₅H₄₂BF₄N₂Pt: C, 59.0; H, 4.6; N, 1.5; P, 6.7. Found: C, 59.5; H, 4.9; N, 1.5; P, 6.0.

Bis(triphenylphosphine)-*N*-acetamidomethylplatinum(II), Pt(CH₃)(NHCOCH₃)(PPh₃)₂ (**35**). A solution of **36** (0.168 g, 0.2 mmol) in acetonitrile (5 mL) was treated with aqueous potassium hydroxide (0.2 mmol). After being stirred for 1 h at room temperature the colorless solution was evaporated to dryness under reduced pressure. The solid residue was washed with water, dried, and recrystallized from benzene to give colorless crystals of **35**, mp 161–163 °C dec, quantitatively. Anal. Calcd for C₃₉H₃₇NOP₂Pt: C, 59.1; H, 4.7; N, 1.8; P, 7.8; mol wt, 793. Found: C, 59.05; H, 5.0; N, 1.65; P, 7.6; mol wt (CHCl₃), 747.

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Reaction of α,α' -Dibromo Ketones and Iron Carbonyls. Mechanistic Aspects^{1,2}

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Abstract: The mechanism of the title reaction has been examined with various substrates and reaction conditions. Reaction of *endo*- α -bromocamphor with $\text{Fe}_2(\text{CO})_9$ in *N,N*-dimethylformamide (DMF) containing 5% of D_2O affords *exo*- α -deuteriocamphor in 80% yield. Debromination of 2,4-dibromo-2,4-dimethylpentan-3-one with $\text{Fe}_2(\text{CO})_9$ in moist DMF proceeds in a stepwise manner, giving first 2-bromo-2,4-dimethylpentan-3-one and then 2,4-dimethylpentan-3-one. Treatment of 1,3-dibromo-1,3-diphenylpropan-2-one with $\text{Fe}_2(\text{CO})_9$ in benzene produces 1-phenyl-2-indanone in 70% yield. Reductive rearrangement of 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one affords 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 95% yield. Reaction of 3,5-dibromo-2,2,6,6-tetramethylheptan-4-one gives a cyclization product, 2-*tert*-butyl-3,3,4-trimethylcyclobutanone, in 78% yield. Reduction of 2,6-dibromo-2,6-di-*tert*-butylcyclohexanone in benzene gives a mixture of 5-*tert*-butyl-1,7,7-trimethylbicyclo[3.2.0]heptan-6-one (80%), 2-*tert*-butyl-6-isopropyl-6-methylcyclohex-2-enone (3%), and 2,6-di-*tert*-butylcyclohex-2-enone (15%). In DMF or tetrahydrofuran (THF), the di-*tert*-butylcyclohexenone is the sole isolable product. 2,6-Dibromo-2,6-diisopropylcyclohexanone upon reaction with $\text{Fe}_2(\text{CO})_9$ in methanol gives 2-methoxy-2,6-diisopropylcyclohexanone (two stereoisomers, 61% yield) along with 2,6-diisopropylcyclohex-2-enone (21%). Reaction of 2,4-dibromo-2,4-dimethylpentan-3-one in the presence of sodium acetate gives 2-acetoxy-2,4-dimethylpentan-3-one (60%) and 2,4-dimethylpent-1-en-3-one (20%). Regioselectivity has been observed in the reaction of an unsymmetrical dibromo ketone. Treatment of 2,4-dibromo-2-methylpentan-3-one with $\text{Fe}_2(\text{CO})_9$ in methanol gives two kinds of methoxy ketones, 2-methoxy-2-methylpentan-3-one and 2-methoxy-4-methylpentan-3-one, in a ratio of 90:10 (45% combined yield); the reduction in DMF containing sodium acetate gives rise to 2-acetoxy-2-methylpentan-3-one and 2-acetoxy-4-methylpentan-3-one in a 69:31 ratio (46% yield) accompanied by a small amount of 2-methylpent-1-en-3-one (<3%) and 2-methylpentan-3-one (9%). These findings indicate that the reaction of dibromo ketones with iron carbonyls produces first enolate intermediates and subsequently reactive oxyallyl-iron(II) species. The latter species, depending on their structures and reaction conditions, experience a variety of cationic rearrangements, nucleophilic trapping, and prototropy forming α,β -unsaturated ketones, etc.

Organic reactions of α -halo ketones have received considerable attention in recent years and proved to be of great synthetic value. The diversity of the chemical reaction is ascribed

to the presence of various functionalities in the molecules, viz., reactive halogen-carbon bond, acidic hydrogen atom, and carbonyl moiety. The halogen atom suffers facile nucleophilic