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Transition Metal–Carbon Bonds. Part XXXIX.[1] Carbonylation and Nuclear Magnetic Resonance Studies on (α-Hydroxyacetylene)bis(triphenylphosphine)platinum Complexes †

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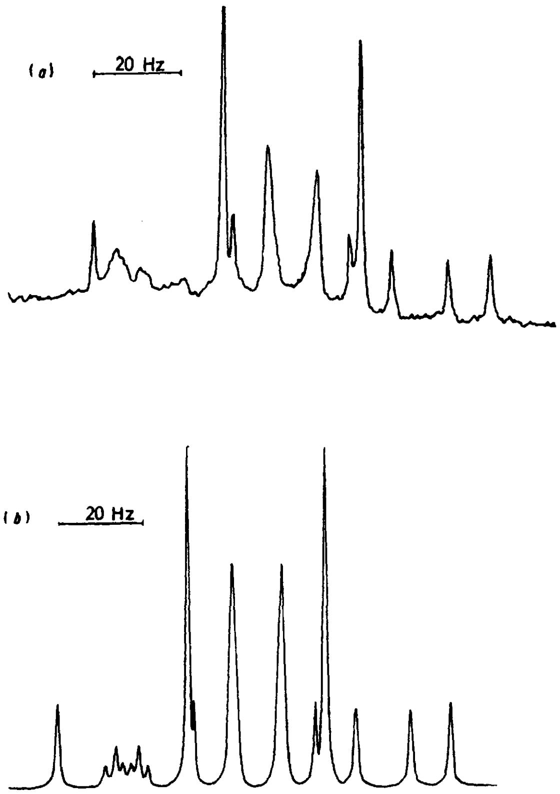
New complexes of the type $[Pt\{R^1C{:}CCR^2R^3(OH)\}(PPh_3)_2]$ (R = H, Ph, or CH_2OH) are described. ^{31}P and ^1H n.m.r. data are given and the ^1H pattern of the methine proton is shown to have more second-order character than previously reported. These complexes carbonylate smoothly to give platinalactone complexes, $[\overline{Pt\{CO\cdot O\cdot CR^2R^3C}{:}CHR^1\}(PPh_3)_2]$, of a new type.

MANY platinum(0)–acetylene(ac) complexes of the type $[Pt(ac)(PPh_3)_2]$ are known.[2-8] They have usually been prepared either by reducing *cis*-$[PtCl_2(PPh_3)_2]$ with hydrazine in the presence of the acetylene or by treating $[Pt(PPh_3)_x]$ ($x = 3$ or 4) with the acetylene. We have found that complexes of this type, where ac = an α-hydroxyacetylene, are readily carbonylated to give a new series of platinalactone complexes. We first describe some new hydroxyacetylene complexes of the type $[Pt\{R^1C{:}CCR^2R^3(OH)\}(PPh_3)_2]$, including a re-interpretation of their ^1H n.m.r. spectra, and then we describe their carbonylation products.

RESULTS AND DISCUSSION

The new acetylene complexes were prepared by the method of Chatt *et al.*[2] They were characterized by microanalytical, i.r., and ^1H and ^{31}P n.m.r. data (Tables 1 and 2). The resonance of the terminal (methine) hydrogen in complexes of the type $[Pt\{HC{:}CCR^2R^3(OH)\}(PPh_3)_2]$ has been previously interpreted[9] as the X part of an AA'X spin system with satellites due to platinum-195, giving an AA'MX system, there being in total 12 lines of relative intensity 1 : 1 : 1 : 1 : 4 : 4 : 4 : 4 : 1 : 1 : 1 : 1. (Approximately one third of the platinum has a spin of one half giving the satellite peaks.) However, we find the spectra are more complicated in particular in the appearance of the low-field set of satellite peaks: the pattern of $[Pt\{HC{:}CCMe_2(OH)\}(PPh_3)_2]$ is typical and is shown in Figure (*a*). The two phosphorus ligand atoms are almost equivalent and the spin systems should be represented as ABX and ABMX. In the ^{31}P n.m.r. spectra, values of $|\delta_{AB}/J_{AB}|$ range from *ca.* 3.5 for the low-field satellites to *ca.* 0.5 for the high-field satellites. The spin system is too complex to analyze fully but the cause of the complex low-field satellite pattern in the ^1H n.m.r. spectrum lies in the relative signs and magnitudes of the coupling constants, the near equivalence of the phosphorus nuclei, and in the coupling of the phosphorus nuclei to the phenyl protons. Thus the computer-simulated spectrum [Figure (*b*)] for the analogous but much simpler spin system shown in (I) has the following shifts and coupling constants: ν(1) 36 432 344.1, ν(2) 36 432 303.3, ν(3) 557.2, ν(4) 657.46, ν(5) 665, and ν(6) 19 350 000; *J*(1,2) 26.9, *J*(1,3) 22.8, *J*(1,4) −4, *J*(1,5) 12, *J*(1,6) 3 554, *J*(2,3) 9.1, *J*(2,4) 12, *J*(2,5) −4, *J*(2,6) 3 448, *J*(3,4) = *J*(3,5) 0, *J*(3,6) −59.8, *J*(4,5) 0, *J*(4,6) 12, *J*(5,6) 12 Hz (linewidths, 1 Hz). These values are, where known, equal to those calculated from the spectrum of $[Pt\{HC{:}CCMe_2(OH)\}(PPh_3)_2]$; values of



^1H N.m.r. patterns at 90 MHz for (*a*) the methine proton of $[Pt\{HC\vdots CCMe_2(OH)\}(PPh_3)_2]$, (*b*) that calculated for the spin system (I) using the parameters given in the text. The system NMRCAL using the Nicolet program NIC-80/S-7117d-B was used

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† No reprints available.

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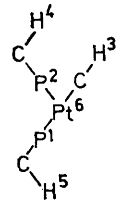
$J(1,4)$, $J(1,5)$, *etc.* were guessed but are similar to what one might expect for the coupling of a phosphorus and an *ortho*-hydrogen atom of a phenyl group. There is a close similarity in the observed [Figure (*a*)] and computer-simulated spectra: the greater complexity of the real spin system would cause further splitting and broadening of the central part of the low-field satellite peaks [Figure (*a*)]. In order to account for the complexity of the low-field satellite peaks in the proton spectrum it is necessary for $^1J(Pt-P_{cis})$ and $^1J(Pt-P_{trans})$ to be opposite in sign to $^2J(Pt-H)$. Other ^1H n.m.r. data for this complex have been reported previously.[9] Our data were obtained by analysis of the resonance patterns as ABX and ABMX spin systems. The ^1H n.m.r. data for the new platinum(O)–acetylene complexes are recorded in Table 2: the methine proton data were calculated by first-order analysis of the central portion of the pattern and of the high-field satellites (second-order analysis changed the values relatively little). Values of $^1J(Pt-P)$ lie in the range 3 406—3 570 and $^2J(P-P)$ in the range 27—32 Hz and are also given in Table 2.



(I)

Carbonylation of the Platinum(O)*-Hydroxyacetylene Complexes*.—Since the platinum(O)-hydroxyacetylene complexes are co-ordinatively unsaturated one might expect them to take up carbon monoxide: the resulting adduct could then undergo further transformations. When carbon monoxide was bubbled through a benzene solution of $[Pt\{HC{:}CCMe_2(OH)\}(PPh_3)_2]$ at *ca.* 20 °C the

TABLE 1

Yield, melting point, analytical,[a] and i.r. data (cm^{-1}) for some platinum(0)–acetylene complexes of the type $[Pt(ac)(PPh_3)_2]$

Complex	Yield (%)	M.p. (θ_c/°C)	Analysis(%) C	Analysis(%) H	$\bar{\nu}(C\equiv C)$ [b]	$\bar{\nu}$(OH) [b]
$[Pt(HC{:}CCH_2OMe)(PPh_3)_2]$ [c]	74	148—153	60.85 (61.0)	4.6 (4.65)	1 710	
$[Pt(HC{:}CCH_2OPh)(PPh_3)_2]$	63	130—131	63.2 (63.45)	4.45 (4.5)	1 718	
$[Pt(HC{:}CCH_2CH_2OH)(PPh_3)_2]$	46	132—134	60.8 (60.85)	4.55 (4.6)	1 712	3 560
$[Pt\{HC{:}CCH(Me)(OH)\}(PPh_3)_2]$	69	143—145	60.8 (60.85)	4.45 (4.6)	1 690	3 600, 3 530
$[Pt\{HC{:}CCH(Ph)(OH)\}(PPh_3)_2]$	41	82—84	63.75 (63.45)	4.75 (4.5)	1 690	3 550
$[Pt\{PhC{:}CCMe_2(OH)\}(PPh_3)_2]$	53	154—156	64.1 (64.15)	4.85 (4.8)	1 765	3 560
$[Pt\{HOCH_2C{:}CCH_2OH\}(PPh_3)_2]$ [c]	55	163—164	59.9 (59.65)	4.6 (4.5)	1 775	3 250
$[Pt\{(HO)CMe_2C{:}CCMe_2(OH)\}(PPh_3)_2]$ [c]	59	152—155	60.95 (61.3)	5.45 (5.15)	1 742	3 210

[a] Calculated values are given in parentheses. [b] As Nujol mulls. [c] Described previously, but the yield, m.p., and n.m.r. data were not given nor were values of $\bar{\nu}$(OH).

TABLE 2

^1H N.m.r.,[a] ^{31}P n.m.r.,[b] and i.r.[c] data for new complexes of type $[Pt\{R^1C{:}CCR^2R^3(OH)\}(PPh_3)_2]$

	^1H				^{31}P			I.r.	
		Other resonances							
	Methine hydrogen [d]	δ	J	Assignment	δ	^1J(Pt–P)	^2J(P–P)	$\bar{\nu}$(C=C)	$\bar{\nu}$(OH)
$[Pt(HC{:}CCH_2OMe)(PPh_3)_2]$	6.65 (*e*,*e*,*e*)	4.04 (d)	^4J(H–H) 1.4	CH_2				1 710	
			^3J(Pt–H) 11.0						
		3.28 (s)		OMe					
$[Pt(HC{:}CCH_2OPh)(PPh_3)_2]$	6.8 (*e*,*e*,*e*)	7.2 (s)		OPh				1 718	
		4.6 (d)	^4J(H–H) 2.1	CH_2					
			^3J(Pt–H) 12.8						
$[Pt(HC{:}CCH_2CH_2OH)(PPh_3)_2]$	6.66 (*e*,*e*,*e*)	3.52	^3J(H–OH) 6.2	CH_2 (β to				1 712	3 560
		(d of t)	^3J(H–H) 5.8	triple bond)					
		2.63	^4J(H–H) 5.6	CH_2 (α to					
		(d of t)	^3J(H–H) 5.8	triple bond)					
			^3J(Pt–H) 34.6						
		1.62 (t)	^3J(H–OH) 6.1	OH					
$[Pt\{HC{:}CCH(Me)(OH)\}(PPh_3)_2]$	6.42 (56.4,	4.7 (q)	^3J(H–H) 6.5	CH	28.1	3 561	32	1 690	3 600,
	10·4,	1.28 (s)		OH	26.7	3 478			3 530
	21.0) [f]	1.22 (d)	^4J(Pt–H) 5.0						
$[Pt\{HC{:}CCH(Ph)(OH)\}(PPh_3)_2]$	6.4 (59.7,	3.73 (s)	^3J(Pt–H) 11.0	CH	26.8	3 547	27	1 690	3 550
	10.0,	1.68 (s)		OH	25.4	3 479			
	22.3)			CH_3					
$[Pt\{PhC{:}CCMe_2(OH)\}(PPh_3)_2]$		1.32 (s)		OH	26.6	3 482	27	1 765	3 560
		1.34 (s)		CH_3	23.6	3 431			
$[Pt(HOCH_2C{:}CCH_2OH)(PPh_3)_2]$		4.16 (s)	^3J(Pt–H) 9.4	CH_2	26.4	3 501		1 775	3 250
		3.20		OH					
$[Pt\{(HO)CMe_2C{:}CCMe_2(OH)\}(PPh_3)_2]$		2.39 (s)		OH	23.8	3 406		1 742	3 210
		1.13 (s)		CH_3					

[a] In $CDCl_3$ at 90 Mz; δ ±0.01 p.p.m., J ±0.1 Hz. s = singlet, d = doublet, t = triplet, and q = quartet. Multiplicities exclude satellites due to platinum-195 coupling. [b] In $CDCl_3$ at 36.43 Mz with all ^1H nuclei decoupled. Shifts relative to 85% H_3PO_4 (±0.1 p.p.m.), J ±2.5 Hz. [c] In cm^{-1} as Nujol mulls. [d] Values of $^2J(Pt-H)$, $^3J(H-P_{cis})$, and $^3J(H-P_{trans})$, respectively are given in parentheses. [e] Could not be measured. [f] ^3J(H–H) 1.4 Hz.

TABLE 3

Yield, melting point, and analytical data * for the products of the carbonylation of platinum(0)–hydroxyacetylene complexes

Complex	Yield (%)	M.p. (θ_c/°C)	Analysis(%)	
			C	H
$[\mathrm{Pt\{CO{\cdot}O{\cdot}CMe_2C{:}CH_2\}(PPh_3)_2}]$	37	172—175	60.85 (60.6)	4.55 (4.60)
$[\mathrm{Pt\{CO{\cdot}O{\cdot}CMe(Et)C{:}CH_2\}(PPh_3)_2}]$	38	165—167	61.45 (61.1)	4.55 (4.75)
$[\mathrm{Pt\{CO{\cdot}O{\cdot}CH(Me)C{:}CH_2\}(PPh_3)_2}]$	32	176—179	60.4 (60.2)	4.55 (4.45)
$[\mathrm{Pt\{CO{\cdot}O{\cdot}C_6H_{10}C{:}CH_2\}(PPh_3)_2]{\cdot}C_6H_6}$	31	158—161	64.3 (64.5)	5.1 (5.1)
$[\mathrm{Pt\{CO{\cdot}O{\cdot}CH_2C{:}CH(CH_2OH)\}(PPh_3)_2}]$	74	165—169	59.45 (59.05)	4.3 (4.35)

* Calculated values are given in parentheses.

TABLE 4

I.r. (cm^{-1}) (Nujol mull) and ^{31}P n.m.r. data [a] for complexes of type $[\mathrm{Pt(CO{\cdot}O{\cdot}CR^2R^3C{:}CH_2)(PPh_3)_2}]$, (II) and $[\mathrm{Pt\{CO{\cdot}O{\cdot}CH_2C{:}CH(CH_2OH)\}(PPh_3)_2}]$, (III)

R^2	R^3	$\tilde{\nu}$(C=C)	$\tilde{\nu}$(C=O)	$\delta(H_3PO_4)$	^1J(Pt–P)	$\lvert ^2J$(P–P)$\rvert$
H	Me	1 598	1 665	25.4	2 117	8.6
				26.2	2 103	
Me	Me	1 600	1 662	26.0	2 056	8.0
				26.1	2 099	
Me	Et	1 594	1 662	26.2	2 056	8.6
				26.4	2 099	
Cyclohexylidene		1 586	1 658	26.0	2 054	7.0
				26.4	2 086	
Complex (III) [b]		1 608	1 666	26.0	2 091	7.5
				26.2	2 135	

[a] δ relative to 85% H_3PO_4 ($\pm$0.1 p.p.m.), J $\pm$2.5 Hz. [b] $\tilde{\nu}$(O–H) at 3 550 cm^{-1}.

TABLE 5

^{1}H N.m.r. data [a] for the complexes of type $[\mathrm{Pt(CO{\cdot}O{\cdot}CR^2R^3C{:}CH_2)(PPh_3)_2}]$, (II), and $[\mathrm{Pt\{CO{\cdot}O{\cdot}CH_2C{:}CH(CH_2OH)\}(PPh_3)_2}]$, (III)

		H_a	H_b	Other resonances		
R^2	R^3	$\delta(J)$ [b]	$\delta(J)$ [b]	δ	J	Assignment
H	Me	4.05 (59.6, *ca*, 2, 9.5)	5.28 (116, 5.2, 18.5)	4.32 (q)	^3J(H–H) 6.2	CH
				1.46 (d)		CH_3
Me	Me	4.12 (57.1, 2.3, 9.4)	5.41 (118.9, 5.6, 19.0)	1.50 (s)		CH_3
Me	Et	4.26 (59.6, 2.3, 9.4)	5.6 (119.4, 5.4, 18.9)	$\left\{\begin{matrix}1.92\ (q)\\1.95\ (q)\end{matrix}\right.$	$\left.\begin{matrix}^3J(H{-}H)\ 7.3\\^3J(H{-}H)\ 7.3\end{matrix}\right\}$	$\mathit{CH_2}CH_3$
				0.90 (t)		$CH_2\mathit{CH_3}$
				1.37 (s)		CH_3
C_6H_{10}		4.03 (61.0, 2.2, 8.8)	5.33 (118.0, 5.2, 18.9)	1.63 (m)		Cyclohexylidene
Complex (III)		4.9 (62, *c*, 7)		4.42	$^4J(-HP_{cis})$ 1.3	$\mathit{CH_2}$C:
				(d of d)	$^4J(-HP_{trans})$ 5.2	
					^3J(Pt–H) 24	
				3.7	^3J(H–H) 6.5	$\mathit{CH_2}$OH
				(d of d)	$^3J(CH_2$–OH) 6.5	
				1.67 (s) [d]		OH

[a] In $CDCl_3$ at 90 MHz. δ $\pm$0.01 p.p.m. m = multiplet. [b] Values of ^3J(Pt–H), $^4J(H{-}P_{cis})$, and $^4J(H{-}P_{trans})$, respectively, are given in parentheses. [c] Obscured by noise. [d] Disappeared on adding D_2O.

initially colourless solution rapidly turned red, but after 3 h the solution became almost colourless and the colourless crystalline heterocyclic complex $[\mathrm{Pt(CO{\cdot}O{\cdot}CMe_2C{:}CH_2)(PPh_3)_2}]$, (II; R = Me), could be isolated. The platinalactone structure (II) follows from microanalytical i.r., and n.m.r. data (Tables 3—5) and has been confirmed by a single-crystal *X*-ray diffraction study.[10] Other platinum–hydroxyacetylene complexes were similarly converted into platinalactone complexes of type (II). We also carbonylated the but-2-yne-1,4-diol complex to give (III). All the complexes showed well defined i.r. absorption bands due to ν(C=O) at *ca.* 1 660 cm^{-1} and to ν(C=C) and the complex from butynediol showed in addition a peak due to ν(OH). In their ^{31}P n.m.r. spectra, values of ^1J(Pt–P) were low (*ca.* 2 100 Hz) because each phosphorus is *trans* to σ-bonded carbon [which has a strong *trans* influence and causes low values of ^1J(Pt–P) *trans* to itself]. Values of J(P–P) were only 7—8.6 Hz. In the ^{1}H n.m.r. spectra the assignments of resonances to H_a and H_b were made on the basis

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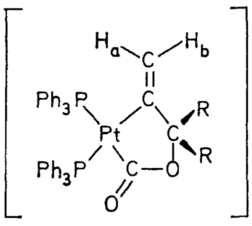
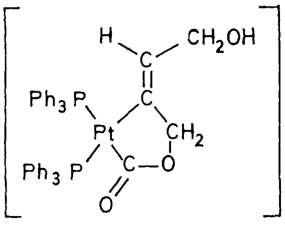
[10] W. S. McDonald and M. C. Norton, unpublished work.

of ^3J(Pt–H) (*trans*) being considerably greater than ^3J(Pt–H) (*cis*). This order of coupling constants, *i.e.* *trans* > *cis*, has been well established for alkenylplatinum(II) complexes.[11]



(II)



(III)

The resonances of both vinylic protons showed a second-order effect, *i.e.* the outer two lines of the quartet were sharper and more intense than the inner lines. As before, this is caused by the near equivalence of the two phosphorus ligand atoms and their coupling to the phenyl hydrogens. For the carbonylation product (III) the value of ^3J(Pt–H$_a$) of 62 Hz shows that the platinum and hydrogen are mutually *cis* on the double bond.

We do not know the mechanism of the carbonylation reaction or the nature of the red intermediate(s). On passing carbon monoxide through a benzene solution of $[Pt\{HC{:}CCMe_2(OH)\}(PPh_3)_2]$ the red solution which developed over a few minutes showed strong bands at *ca.* 1 962 and 1 818 cm^{-1}, presumably due to platinum carbonyl species. These bands gradually decreased in intensity and the final colourless or near colourless solution showed strong absorptions due to the platinalactone (II) at 1 675 cm^{-1} and carbonyl bands at 1 990 and 1 945, possibly due to $[Pt(CO)_2(PPh_3)_2]$,[12] and a medium absorption at 2 085 cm^{-1} which we have not assigned.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R12A spectrometer at *ca.* 35 °C and 60 MHz or on a Bruker HFX spectrometer at 90 MHz and ambient temperatures. ^{31}P N.m.r. spectra were also obtained on the Bruker HFX spectrometer at 36.43 MHz. Infrared spectra were recorded on Perkin-Elmer model 457 (250—4 000 cm^{-1}) or Grubb-Parsons DB3/DN2 (200—500 cm^{-1}) spectrometers.

Preparation of the Platinum(0)*-Hydroxyacetylene Complexes.*— $[Pt\{HC{:}CCH(Me)(OH)\}(PPh_3)_2]$. *cis*-Dichlorobis(triphenylphosphine)platinum(II) (0.30 g, 0.39 mmol) was slurried in ethanol (10 cm^3). Hydrazine hydrate was added dropwise while warming, until a yellow solution resulted. The solution was filtered and HC:CCH(Me)(OH) (0.16 g, 2.34 mmol) added. The resulting colourless solution was warmed for 2 min. When the solution cooled to room temperature, white needles of $[Pt\{HC{:}CCH(Me)(OH)\}(PPh_3)_2]$ (0.22 g, 0.27 mmol, 69%) separated.

The following complexes were prepared in a similar manner: $[Pt(HC{:}CCH_2OMe)(PPh_3)_2]$; $[Pt(HC{:}CCH_2OPh)(PPh_3)_2]$; $[Pt(HC{:}CCH_2CH_2OH)(PPh_3)_2]$; $[Pt\{HC{:}CCH(Ph)(OH)\}(PPh_3)_2]$; $[Pt\{PhC{:}CCMe_2(OH)\}(PPh_3)_2]$; $[Pt(HOCH_2C{:}CCH_2OH)(PPh_3)_2]$; and $[Pt\{(HO)CMe_2C{:}CCMe_2(OH)\}(PPh_3)_2]$. All the complexes are white.

Carbonylation of Platinum(0)*-Hydroxyacetylene Complexes.—Preparation of* $[Pt(CO{\cdot}O{\cdot}CMe_2C{:}CH_2)(PPh_3)_2]$. Carbon monoxide was bubbled through a colourless solution of $[Pt\{HC{:}CCMe_2(OH)\}(PPh_3)_2]$ (0.30 g, 0.36 mmol) in benzene (10 cm^3). After 5 min the solution became dark red; after 3 h a very pale yellow solution resulted. The solution was reduced in volume under reduced pressure and n-hexane was added. The light brown precipitate that formed was filtered off and washed with acetone to give a white solid, $[Pt(CO{\cdot}O{\cdot}CMe_2C{:}CH_2)(PPh_3)_2]$ (0.11 g, 0.13 mmol, 37%). The complex formed white prisms from benzene–hexane.

The following white complexes can be prepared in a similar manner: $[Pt\{CO{\cdot}O{\cdot}CMe(Et)C{:}CH_2\}(PPh_3)_2]$; $[Pt(CO{\cdot}O{\cdot}C_6H_{10}C{:}CH_2)(PPh_3)_2]$; and $[Pt\{CO{\cdot}O{\cdot}CH(Me)C{:}CH_2\}(PPh_3)_2]$.

Preparation of $[Pt\{CO{\cdot}O{\cdot}CH_2C{:}CH(CH_2OH)\}(PPh_3)_2]$, (III).—Carbon monoxide was bubbled through a colourless solution of $[Pt(HOCH_2C{:}CCH_2OH)(PPh_3)_2]$ (0.46 g, 0.58 mmol) in benzene (15 cm^3). After 5 min the solution became pale yellow, and after 4 h the solution was almost colourless. Addition of n-hexane to this solution gave $[Pt\{CO{\cdot}O{\cdot}CH_2C{:}CH(CH_2OH)\}(PPh_3)_2]$ (0.36 g, 0.43 mmol, 74%). The complex crystallizes as white prisms from benzene–hexane.

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