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Synthesis, Characterization, and Structure of Tungsten-Pentadienyl Compounds. An Observable $\eta^5 \rightleftarrows \eta^3$ Equilibrium for a Pentadienyl Ligand

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The reaction between $W(CO)_3(CH_3CN)_3$ and 1-bromopenta-2,4-diene produces $(\eta^3\text{-}C_5H_7)W(CO)_2(CH_3CN)_2Br$ (**1a**). Addition of bis(diphenylphosphino)ethane (dppe) and bis(dimethylphosphino)ethane (dmpe) to **1a** in CH_2Cl_2 gives $W(\overset{\frown}{P\ P})(CO)_2$(*syn*-$\eta^3$-pentadienyl)Br ($\overset{\frown}{P\ P}$ = dppe (**1b**), dmpe (**1c**)) in high yields. Stirring of **1b** and **1c** each with 1 equiv of $AgPF_6$ in CH_2Cl_2 yields the cations $[(\eta^5\text{-}C_5H_7)W(CO)_2(\overset{\frown}{P\ P})]PF_6$ ($\overset{\frown}{P\ P}$ = dppe (**2a**), dmpe (**2b**)). In CH_3CN, **2a** and **2b** each undergoes rearrangement to produce the corresponding cations $[(\eta^3\text{-}C_5H_7)W(CO)_2(\overset{\frown}{P\ P})(CH_3CN)]PF_6$ ($\overset{\frown}{P\ P}$ = dppe (**3a**), dmpe (**3b**)). In CH_2Cl_2 and CH_3COCH_3, the η^3-cations **3a** and **3b** readily lose CH_3CN to re-form **2a** and **2b** and reach equilibrium. The equilibrium constants $K_{eq} = [\eta^5][CH_3CN]/[\eta^3]$ for this $\eta^3 \rightleftarrows \eta^5$ reversible process were determined from ^{31}P NMR spectroscopy in CD_2Cl_2 and CD_3COCD_3. Measurement of K_{eq} from −10 to +20 °C in CD_2Cl_2 gives $\Delta H = 10.6 \pm 0.2$ kcal mol^{-1} and $\Delta S = 29.0 \pm 1.2$ eu (eu = entropy unit) for **3a** $\rightleftarrows$ **2a** + CH_3CN and $\Delta H = 8.2 \pm 0.3$ kcal mol^{-1} and $\Delta S = 29.4 \pm 1.3$ eu for **3b** $\rightleftarrows$ **2b** + CH_3CN. The molecular structures of **1c** and **2a** have been determined from an X-ray diffraction study. Crystallographic data: **1c** space group *Pbca*, $a = 12.400$ (5) Å, $b = 13.226$ (4) Å, $c = 22.100$ (6) Å, $Z = 8$, $R = 0.0326$, and $R_w = 0.0333$; **2a** space group $P\bar{1}$, $a = 11.047$ (4) Å, $b = 11.457$ (4) Å, $c = 14.311$ (5) Å, $\alpha = 86.08$ (3)°, $\beta = 80.53$ (3)°, $\gamma = 66.19$ (3)°, $Z = 2$, $R = 0.0268$, and $R_w = 0.0274$.

Introduction

The $\eta^5 \rightleftarrows \eta^3$ ring slippage of transition-metal–cyclopentadienyl and –indenyl complexes is of particular interest because of its role in various chemical reactions.[1] Recent papers[2,3] have demonstrated that this process is a key step in the mechanism of CO insertion into metal–alkyl bonds, α-hydrogen abstraction, β-hydrogen elimination, C–H and C–C bond scission, ligand substitution, and cyclopentadienyl ligand transfer.

In recent years,[4-6] there has been a resurgence of interest in the chemistry of acyclic transition-metal–pentadienyl complexes. Theoretical studies have shown that the resonance energy of a η^5-pentadienyl group is smaller than that of a η^5-cyclopentadienyl group, and hence the $\eta^5 \rightleftarrows \eta^3$ interconversion should be more facile for the metal–pentadienyl system. In the metal–pentadienyl system, the interconversion between the η^5 and η^3 modes has been observed in several studies.[7-9] Nevertheless, none of the cases above is an equilibrium system. In this paper, we report a reversible $\eta^5 \rightleftarrows \eta^3$ rearrangement involving the complexes $[(\eta^5\text{-}C_5H_7)W(CO)_2(\overset{\frown}{P\ P})]^+$ and $[(\eta^3\text{-}C_5H_7)W(CO)_2(\overset{\frown}{P\ P})(CH_3CN)]^+$. One interesting feature of this interconversion is that the system is observed to be in a state of equilibrium between the two forms. In order to demonstrate the facile nature of the $\eta^5 \rightleftarrows \eta^3$ interconversion in this system, we have obtained the equilibrium constants K_{eq} as well as the thermal parameters ΔH and ΔS.

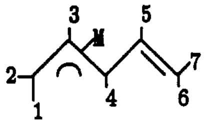
Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of **1c**

	x	*y*	*z*	*U*(eq)[a]
W	94 (1)	2465 (1)	1160 (1)	34 (1)
Br	−248 (1)	2729 (1)	2370 (1)	60 (1)
P(1)	491 (3)	642 (2)	1404 (2)	45 (1)
P(2)	−1730 (2)	1703 (2)	1260 (1)	42 (1)
O(1)	403 (8)	1928 (8)	−154 (4)	76 (4)
O(2)	−1395 (9)	4035 (7)	511 (5)	95 (5)
C(1)	279 (10)	2134 (10)	325 (6)	52 (5)
C(2)	−834 (10)	3495 (9)	773 (6)	61 (5)
C(3)	2024 (9)	2473 (11)	1145 (9)	79 (6)
C(4)	1643 (10)	3289 (10)	1388 (7)	67 (5)
C(5)	1032 (10)	4053 (9)	1113 (7)	63 (6)
C(6)	695 (11)	4961 (11)	1387 (10)	93 (8)
C(7)	506 (13)	5838 (12)	1164 (8)	91 (8)
C(8)	−747 (10)	−106 (9)	1465 (7)	68 (6)
C(9)	−1657 (10)	525 (8)	1676 (6)	68 (6)
C(10)	1203 (12)	−78 (9)	838 (7)	86 (7)
C(11)	1265 (10)	361 (9)	2079 (5)	68 (5)
C(12)	−2406 (9)	1381 (9)	584 (6)	75 (6)
C(13)	−2765 (9)	2432 (9)	1622 (6)	78 (5)

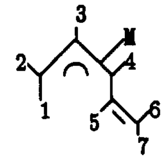
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

Synthesis of $(\eta^3\text{-}C_5H_7)W(CO)_2L_2Br$ (L_2 = 2 CH_3CN, dppe, dmpe). The reaction between $W(CO)_3(CH_3CN)_3$ and 1-bromopenta-2,4-diene led to the formation of the complex $(\eta^3\text{-}C_5H_7)W(CO)_2(CH_3CN)_2Br$ (**1a**) in high yield. Complex **1a** forms red rodlike crystals after slow evaporation of a saturated CH_3CN solution. The ^1H NMR spectrum of **1a** in CD_3CN at −60 °C reveals that the pentadienyl ligand adopts a syn-η^3 configuration, as revealed by the coupling constants $J_{13} = J_{34} = 10.0$ Hz and $J_{23} = 7.0$ Hz. The anti geometry is expected to have the coupling constant $J_{34} = J_{23} = 6.7$ Hz. The two CH_3CN ligands in **1a** are readily displaced by a bidentate phosphine ligand. Addition of bis(diphenylphosphino)ethane (dppe) and bis(dimethylphosphino)ethane (dmpe) to **1a** in CH_2Cl_2 produced $W(\overset{\frown}{P\ P})(CO)_2$(*syn*-$\eta^3$-pentadienyl)Br ($\overset{\frown}{P\ P}$ = dppe (**1b**), dmpe (**1c**)) in high yield. Compounds **1b** and **1c** were obtained as red block crystals after crystallization from a saturated $CHCl_3$/diethyl ether solution. In solution, only the syn isomer was detectable for **1b** and **1c** by ^1H NMR spectroscopy. The solution IR spectra exhibit two carbonyl absorption bands of equal intensity, indicative of cis carbonyl ligands. ^{31}P NMR spectra show an AB quartet with ^{183}W satellites J_{PW} = 180–190 Hz and J_{PP} = 23 Hz.



syn-η^3



anti-η^3

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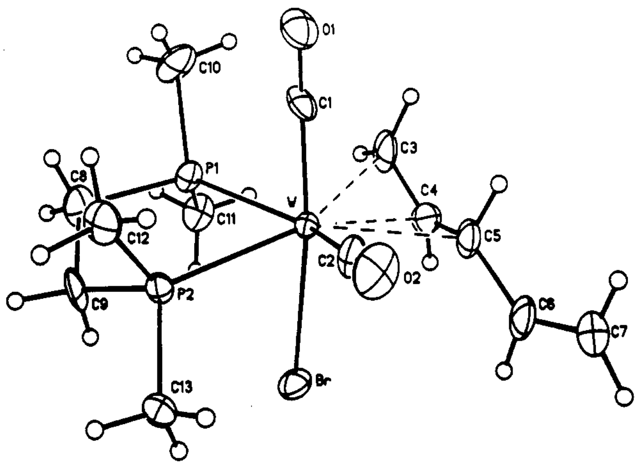

Figure 1. ORTEP drawing of $W(CO)_2(dmpe)Br(\eta^3\text{-}C_5H_7)$.

Table II. Selected Bond Distances (Å) and Angles (deg) of **1c**

W–Br	2.730 (2)	W–P(1)	2.519 (3)
W–P(2)	2.486 (3)	W–C(1)	1.911 (12)
W–C(2)	1.978 (13)	W–C(3)	2.393 (11)
W–C(4)	2.265 (13)	W–C(5)	2.404 (12)
P(1)–C(8)	1.831 (13)	P(1)–C(10)	1.802 (14)
P(1)–C(11)	1.812 (13)	P(2)–C(9)	1.810 (12)
P(2)–C(12)	1.765 (13)	P(2)–C(13)	1.792 (12)
O(1)–C(1)	1.103 (16)	O(2)–C(2)	1.152 (16)
C(3)–C(4)	1.294 (20)	C(4)–C(5)	1.402 (19)
C(5)–C(6)	1.409 (21)	C(6)–C(7)	1.282 (23)
C(8)–C(9)	1.479 (18)		
Br–W–P(1)	86.8 (1)	Br–W–P(2)	79.8 (1)
P(1)–W–P(2)	76.8 (1)	Br–W–C(1)	173.8 (4)
P(1)–W–C(1)	87.9 (4)	P(2)–W–C(1)	95.9 (4)
Br–W–C(2)	104.2 (4)	P(1)–W–C(2)	149.9 (4)
P(2)–W–C(2)	77.8 (4)	C(1)–W–C(2)	79.0 (6)
Br–W–C(3)	99.7 (5)	P(1)–W–C(3)	79.2 (4)
P(2)–W–C(3)	155.9 (4)	C(1)–W–C(3)	82.4 (6)
C(2)–W–C(3)	124.9 (5)	Br–W–C(4)	81.6 (4)
P(1)–W–C(4)	104.3 (4)	P(2)–W–C(4)	161.3 (4)
C(1)–W–C(4)	102.8 (5)	C(2)–W–C(4)	105.0 (5)
C(3)–W–C(4)	32.1 (5)	Br–W–C(5)	90.4 (3)
P(1)–W–C(5)	138.7 (3)	P(2)–W–C(5)	143.0 (3)
C(1)–W–C(5)	95.7 (5)	C(2)–W–C(5)	70.2 (5)
C(3)–W–C(5)	60.8 (5)	C(4)–W–C(5)	34.8 (5)
W–P(1)–C(8)	111.7 (4)	W–P(1)–C(10)	116.9 (4)
C(8)–P(1)–C(10)	100.2 (6)	W–P(1)–C(11)	118.4 (4)
C(8)–P(1)–C(11)	105.8 (6)	C(10)–P(1)–C(11)	101.7 (6)
W–P(2)–C(9)	110.4 (4)	W–P(2)–C(12)	117.0 (4)
C(9)–P(2)–C(12)	104.2 (6)	W–P(2)–C(13)	118.2 (4)
C(9)–P(2)–C(13)	105.8 (6)	C(12)–P(2)–C(13)	99.7 (6)
W–C(1)–O(1)	178.4 (11)	W–C(2)–O(2)	174.4 (11)
W–C(3)–C(4)	68.5 (7)	W–C(4)–C(3)	79.4 (8)
W–C(4)–C(5)	78.0 (8)	C(3)–C(4)–C(5)	128.2 (15)
W–C(5)–C(4)	67.2 (7)	W–C(5)–C(6)	125.6 (10)
C(4)–C(5)–C(6)	126.1 (15)	C(5)–C(6)–C(7)	131.3 (20)
P(1)–C(8)–C(9)	111.0 (8)	P(2)–C(9)–C(8)	111.4 (9)

The molecular structure of **1c** has been characterized by an X-ray diffraction study. The ORTEP drawings of the molecular structure are given in Figure 1, and the atomic coordinates and bond distances and angles are given in Tables I and II, respectively. The coordination geometry can be described as pseudooctahedral if the allyl group is considered to occupy one coordination site. An equatorial plane is defined by the two phosphorus atoms, C(2)–O(2), and the centroid of the allyl group, with a maximum deviation of 0.359 Å. The C(1)–O(1) and bromide ligands occupy the axial sites. The angle P(1)–W–P(2) is 76.8 (1)°, which indicates distortion from an ideal octahedron structure. The pentadienyl group is planar with a dihedral angle between the allylic plane C(3)–C(4)–C(5) and vinylic plane C(5)–C(6)–C(7) of 27.2°. The carbon atoms C(3)–C(4)–C(5)–C(6) of the pentadienyl group form a least-squares plane with a maximum deviation of about 0.022 Å, while the C(7) atom lies out of this plane at a distance of 0.499 Å. The mouth of the allyl group faces the two carbonyls. The tungsten atom is asymmetrically bonded to the allylic moiety with W–C(3) (2.393 (11) Å), W–C(4) (2.265 (13) Å), and W–C(3) (2.404 (12) Å). The W(1)–P(1) (2.499 (2) Å) bond distance is comparable to that (2.526 (2) Å) of the W(1)–P(2) bond.

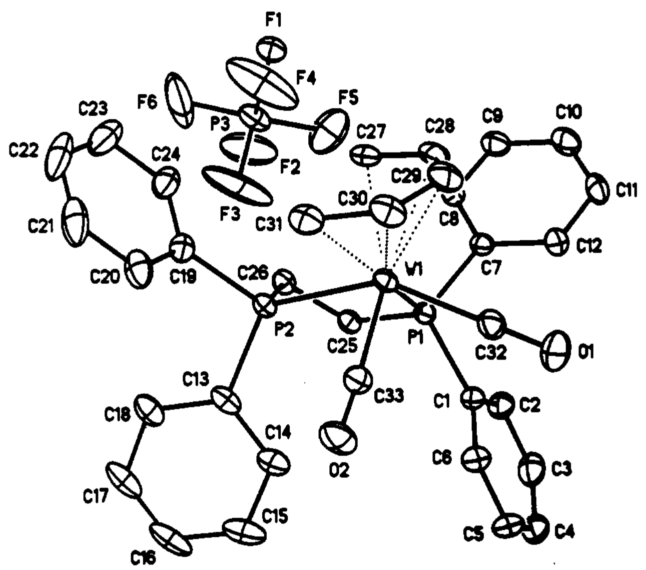

Figure 2. ORTEP drawing of the $[W(CO)_2(dppe)(\eta^5\text{-}C_5H_7)]^+$ cation.

Synthesis of the (η^5-C_5H_7)W(CO)$_2$($P^\frown P$) Cations ($P^\frown P$ = dppe, dmpe). Stirring of **1b** and **1c** with 1 equiv of $Ag[PF_6]$ in CH_2Cl_2 gave the cations $[(\eta^5\text{-}C_5H_7)W(CO)_2(P^\frown P)]PF_6$ ($P^\frown P$ = dppe (**2a**), dmpe (**2b**)) in good yields after workup. Recrystallization from a saturated CH_2Cl_2/ether solution produced yellow crystals of **2a** and orange crystals of **2b**. Compounds **2a** and **2b** have a U-shaped pentadienyl group as indicated by the upfield chemical shifts of the two anti protons H^1 and H^7, δ 0.5–1.0 ppm. An X-ray diffraction study of **2a** was performed to elucidate the molecular structure. An ORTEP drawing is shown in Figure 2, and the atomic coordinates and selected bond distances and angles are given in Tables III and IV, respectively. The coordination geometry about the tungsten atom is a distorted square pyramid with the P(1), P(2), C(32), and C(33) atoms occupying the four basal sites. One chelating phosphorus atom is situated beneath the open mouth of the dienyl ligand, whereas the other lies below the edge. An interesting feature is that the P(2)–W–C(32) atoms lie on a line that nearly bisects the pentadienyl plane. Such a stereochemistry fully agrees with the predicted geometry for the $(\eta^5\text{-}C_5H_7)ML_4$ system.[10a] Bond lengths for W–P(1) and W–P(2) are 2.499 (2) and 2.526 (2) Å, respectively. The C(30) atom is within 0.03 Å of the plane defined by atoms C(27)–C(29). The distances between the tungsten atom and the five carbons of the pentadienyl group are 2.319 (6)–2.368 (5) Å; these bond distances are nearly equal to those (2.29 (2)–2.37 (2) Å) of the neutral W–dienyl complex (I).[10b] In **2a**, the C–C bond distances in the C(27)–C(31) fragment, 1.386 (13)–1.443 (9) Å, are comparable to the corresponding distances of molecule I (1.386 (13)–1.443 (9) Å). The P(1) atom is 3.296 Å from the pentadienyl plane compared with 2.113 Å for the P(2) atom.

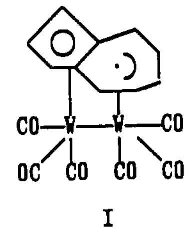

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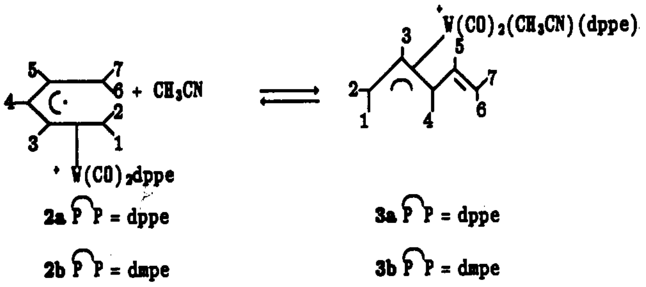
Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) of **2a**

	x	*y*	*z*	*U*(eq)[a]
W(1)	11698 (1)	2139 (1)	2917 (1)	38 (1)
P(1)	11702 (1)	3984 (1)	1881 (1)	38 (1)
P(2)	9595 (1)	2771 (1)	2178 (1)	39 (1)
P(3)	6144 (2)	7910 (2)	3235 (1)	75 (1)
F(1)	5627 (4)	8991 (4)	3991 (3)	83 (2)
F(2)	5646 (8)	8906 (6)	2465 (4)	176 (4)
F(3)	6648 (9)	6847 (6)	2497 (6)	253 (5)
F(4)	6649 (13)	6936 (6)	4005 (6)	255 (8)
F(5)	7480 (6)	8027 (11)	3109 (7)	249 (7)
F(6)	4738 (8)	7900 (8)	3384 (7)	216 (6)
O(1)	14737 (5)	1651 (5)	2404 (4)	88 (3)
O(2)	12630 (5)	−324 (4)	1707 (4)	81 (2)
C(1)	12955 (5)	3758 (6)	822 (4)	49 (3)
C(2)	13073 (6)	4807 (7)	349 (4)	60 (3)
C(3)	13941 (7)	4654 (9)	−504 (5)	77 (4)
C(4)	14679 (8)	3463 (10)	−877 (5)	85 (5)
C(5)	14557 (7)	2440 (9)	−417 (6)	91 (4)
C(6)	13709 (6)	2561 (7)	440 (4)	66 (3)
C(7)	11838 (5)	5251 (5)	2520 (4)	41 (2)
C(8)	10712 (6)	6311 (5)	2870 (4)	48 (2)
C(9)	10845 (7)	7212 (6)	3399 (4)	62 (3)
C(10)	12074 (8)	7063 (6)	3570 (5)	68 (4)
C(11)	13199 (7)	6014 (7)	3238 (5)	64 (3)
C(12)	13087 (6)	5106 (6)	2710 (4)	54 (3)
C(13)	9632 (6)	2141 (5)	1031 (4)	52 (3)
C(14)	10744 (7)	1879 (6)	336 (4)	61 (3)
C(15)	10690 (10)	1564 (7)	−579 (5)	84 (4)
C(16)	9566 (11)	1499 (7)	−792 (6)	93 (5)
C(17)	8470 (10)	1719 (7)	−104 (6)	88 (5)
C(18)	8473 (7)	2060 (6)	801 (5)	67 (3)
C(19)	8230 (6)	2506 (6)	2934 (4)	50 (3)
C(20)	8272 (8)	1292 (7)	3011 (5)	73 (4)
C(21)	7284 (10)	1051 (10)	3613 (7)	103 (6)
C(22)	6292 (10)	1977 (13)	4139 (7)	119 (7)
C(23)	6257 (8)	3190 (11)	4086 (6)	101 (5)
C(24)	7231 (6)	3480 (7)	3481 (5)	68 (3)
C(25)	10140 (5)	4756 (5)	1360 (4)	43 (2)
C(26)	8995 (5)	4481 (5)	1933 (4)	44 (2)
C(27)	10226 (6)	3664 (6)	4063 (4)	54 (3)
C(28)	11512 (7)	3184 (6)	4311 (4)	59 (3)
C(29)	12323 (8)	1846 (7)	4424 (4)	69 (3)
C(30)	12035 (7)	822 (6)	4238 (4)	64 (3)
C(31)	10808 (7)	945 (6)	3988 (4)	62 (3)
C(32)	13625 (7)	1810 (6)	2603 (4)	58 (3)
C(33)	12308 (6)	604 (6)	2126 (4)	52 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I



Discussion

Reversible $\eta^5 \rightleftarrows \eta^3$ Equilibrium. An interesting feature of cations **2a** and **2b** is their facile rearrangement to the η^3-cations promoted by CH_3CN (Scheme I). When crystals of **2a** and **2b** were dissolved in CH_3CN, new CO absorptions in the IR spectrum appeared at ~1945 (s) and ~1865 (s) cm^{-1}, concurrently with the disappearance of ν(CO) bands at ~1985 (s) and ~1920 (s) cm^{-1} assignable to the η^5-cations. The two new absorptions at ~1945 (s) and ~1865 (s) cm^{-1} are due to the ν(CO) absorptions of $[(syn\text{-}\eta^3\text{-}C_5H_7)W(CO)_3(\overset{\frown}{P\ P})(CH_3CN)]PF_6$ ($\overset{\frown}{P\ P}$ = dppe (**3a**), dmpe (**3b**)). Isolation of **3a** and **3b** was achieved by removal of CH_3CN, followed by recrystallization from a saturated CH_3CN/diethyl ether solution. Elemental analyses and IR, ^1H and NMR and ^{31}P NMR spectra were compatible with the given formula. The *syn*-η^3-pentadienyl configuration is indicated by the ^1H NMR coupling constants, $J_{13} = J_{34} = 10.4$ Hz and $J_{23} = 7.0$ Hz. These η^3-cations can be alternatively prepared from the reaction between **1b** and $AgPF_6$ in CH_3CN; the yield is 85%.

Table IV. Selected Bond Distances (Å) and Angels (deg) of **2a**

W(1)–P(1)	2.499 (2)	W(1)–P(2)	2.526 (2)
W(1)–C(27)	2.368 (5)	W(1)–C(28)	2.334 (7)
W(1)–C(29)	2.334 (7)	W(1)–C(30)	2.319 (6)
W(1)–C(31)	2.343 (7)	W(1)–C(32)	1.984 (7)
W(1)–C(33)	1.972 (6)	P(1)–C(1)	1.832 (5)
P(1)–C(7)	1.834 (7)	P(1)–C(25)	1.849 (6)
P(2)–C(13)	1.826 (7)	P(2)–C(19)	1.823 (7)
P(2)–C(26)	1.826 (5)	O(1)–C(32)	1.155 (9)
O(2)–C(33)	1.153 (8)	C(27)–C(28)	1.398 (10)
C(28)–C(29)	1.443 (9)	C(29)–C(30)	1.386 (13)
C(30)–C(31)	1.409 (12)		

P(1)–W(1)–P(2)	76.8 (1)	P(1)–W(1)–C(27)	86.8 (2)
P(2)–W(1)–C(27)	82.2 (2)	P(1)–W(1)–C(28)	93.7 (2)
P(2)–W(1)–C(28)	116.8 (2)	C(27)–W(1)–C(28)	34.6 (2)
P(1)–W(1)–C(29)	122.5 (2)	P(2)–W(1)–C(29)	138.6 (2)
C(27)–W(1)–C(29)	64.7 (2)	C(28)–W(1)–C(29)	36.0 (2)
P(1)–W(1)–C(30)	157.1 (2)	P(2)–W(1)–C(30)	121.0 (2)
C(27)–W(1)–C(30)	82.0 (2)	C(28)–W(1)–C(30)	66.0 (2)
C(29)–W(1)–C(30)	34.7 (3)	P(1)–W(1)–C(31)	157.5 (1)
P(2)–W(1)–C(31)	85.9 (2)	C(27)–W(1)–C(31)	76.7 (2)
C(28)–W(1)–C(31)	81.3 (3)	C(29)–W(1)–C(31)	63.7 (3)
C(30)–W(1)–C(31)	35.2 (3)	P(1)–W(1)–C(32)	76.6 (2)
P(2)–W(1)–C(32)	142.2 (2)	C(27)–W(1)–C(32)	122.2 (3)
C(28)–W(1)–C(32)	91.2 (3)	C(29)–W(1)–C(32)	78.9 (3)
C(30)–W(1)–C(32)	92.6 (3)	C(31)–W(1)–C(32)	125.2 (2)
P(1)–W(1)–C(33)	109.1 (2)	P(2)–W(1)–C(33)	83.2 (2)
C(27)–W(1)–C(33)	155.3 (3)	C(28)–W(1)–C(33)	153.0 (2)
C(29)–W(1)–C(33)	117.0 (2)	C(30)–W(1)–C(33)	88.5 (2)
C(31)–W(1)–C(33)	82.5 (2)	C(32)–W(1)–C(33)	80.8 (3)
W(1)–P(1)–C(1)	120.9 (2)	W(1)–P(1)–C(7)	113.0 (2)
C(1)–P(1)–C(7)	103.0 (3)	W(1)–P(1)–C(25)	111.8 (2)
C(1)–P(1)–C(25)	100.7 (2)	C(7)–P(1)–C(25)	105.6 (2)
W(1)–P(2)–C(13)	121.3 (2)	W(1)–P(2)–C(19)	114.5 (2)
C(13)–P(2)–C(19)	103.7 (3)	W(1)–P(2)–C(26)	107.6 (2)
C(13)–P(2)–C(26)	101.5 (3)	C(19)–P(2)–C(26)	106.8 (2)
P(1)–C(25)–C(26)	111.9 (4)	P(2)–C(26)–C(25)	108.5 (3)
W(1)–C(27)–C(28)	71.4 (3)	W(1)–C(28)–C(27)	74.0 (4)
W(1)–C(28)–C(29)	72.0 (4)	C(27)–C(28)–C(29)	124.5 (8)
W(1)–C(29)–C(28)	72.0 (4)	W(1)–C(29)–C(30)	72.1 (4)
C(28)–C(29)–C(30)	127.2 (7)	W(1)–C(30)–C(29)	73.3 (4)
W(1)–C(30)–C(31)	73.3 (4)	C(29)–C(30)–C(31)	123.9 (6)
W(1)–C(31)–C(30)	71.5 (4)	W(1)–C(32)–O(1)	177.9 (5)
W(1)–C(33)–O(2)	176.0 (6)		

The two η^3-cations are prone to loss of the coordinated CH_3CN in solvents other than acetonitrile and re-form the η^5-cations **2a** and **2b**, respectively. When **3a** was dissolved in CD_2Cl_2 and CD_3COCD_3 and the solution was monitored by IR and NMR spectroscopy, the signals of **2a** began to appear slowly with liberation of free CH_3CN. An equilibrium was reached in 10 h. A similar $\eta^5 \rightleftarrows \eta^3$ equilibrium was observed when **3b** was dissolved in CD_2Cl_2 or CD_3COCD_3 solution. As the interconversion was found to be in a state of dynamic equilibrium, the equilibrium constants *K* (mol/L), defined by the equation $K_{eq} = [\eta^5][CH_3CN]/[\eta^3 - CH_3CN]$ could be estimated by the NMR integral. A more precise measurement was obtained from the ^{31}P NMR spectra, which show the resonances for the two nonequivalent phosphorus atoms as a well-defined AB pattern in addition to the ^{183}W satellite (J_{WP} = 200–210 Hz). At 23 °C, the equilibrium constants for **3a** $\rightleftarrows$ **2a** + CH_3CN was determined to be $(3.35 \pm 0.02) \times 10^{-3}$ M in CD_2Cl_2; whereas for **3b** $\rightleftarrows$ **2b** + CH_3CN, the $K = 2.42 \pm 0.02$ M in CD_2Cl_2.

Over an appropriate temperature range −10 to +20 °C, pertinent plots of ln K_{eq} vs $1/T$ have been prepared. To test the overall reliability of the thermodynamic parameters, measurements were carried out on three independent runs. In the particular case of **3a** $\rightleftarrows$ **2a** + CH_3CN, the respective ΔH values of three runs for both **2a** and **2b** are 10.6 ± 0.2, 10.4 ± 0.2, and 10.7 ± 0.2 kcal

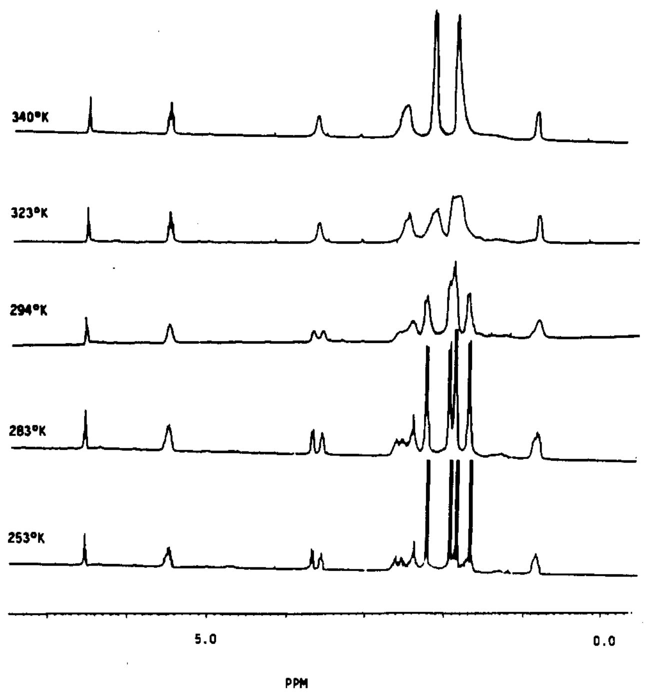
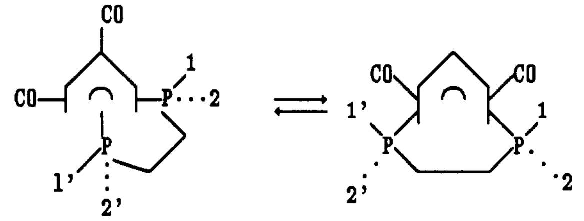


Figure 3. Variable-temperature ^{1}H NMR spectrum of [W(η^5-C_5H_7)-$(CO)_2$(dmpe)]$^+$.

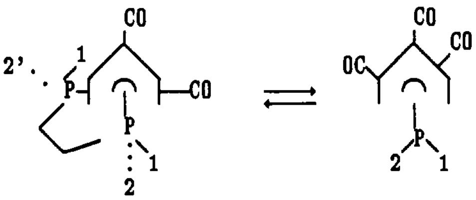
mol^{-1}, while the respective ΔS values are 28.2 ± 1.1, 29.6 ± 1.2, and 29.2 ± 1.2 eu (eu = entropy unit). These three independent runs produce a mean value of ΔH = 10.6 ± 0.2 kcal mol^{-1} and ΔS = 29.0 ± 1.2 eu. For the **3b** $\rightleftarrows$ **2b** + CH_3CN equilibrium, the linear plot of ln K_{eq} versus $1/T$ produces a mean value of ΔH = 8.2 ± 0.3 kcal mol^{-1} and ΔS = 29.4 ± 1.5 eu based on three independent runs. For these systems, the similar ΔS values might reflect the reliability of the data.[11] It is of interest to compare the ΔH and K_{eq} values between the η^5-dppe (**2a**) and η^5-dmpe (**2b**) complexes. The data above implies that the bidentate dmpe ligand tends to stabilize the η^5-structure more effectively than the dppe ligand. This observation can be tentatively explained by both electronic and steric effects. The increase of the metal electron density by the dmpe ligand may contribute to the strength of metal-ligand bonding through donation of metal d electrons to the empty ligand orbital. We do not preclude the possibility that the more congested structure of **3a** tends to favor the $\eta^5 \rightarrow \eta^3$ slippage.

Dynamic NMR Studies. The NMR spectra of **2a** and **2b** at ambient temperatures are consistent with the asymmetric orientation of the pentadienyl and bis(phosphino) ligands, as observed in the solid-state structure. The two ends of the chelating phosphines and the two ends of the pentadienyl protons are inequivalent. The $^{31}\{^1H\}$ NMR spectra exhibit a distinct AB quartet pattern, and the ^{1}H NMR spectra exhibit seven distinct signals for the pentadienyl protons. However, with increase of temperatures, the rate of the pentadienyl rotation with respect to the bis(phosphino) fragment increases. The AB pattern in the ^{31}P NMR spectrum begins to broaden and to coalesce to one resonance with a ^{183}W-P satellite (J_{WP} = 200 Hz). Similar behavior is observed in the temperature-dependent ^{1}H NMR spectra of the pentadienyl hydrogens. Notably, for **2b**, in the δ 1.50–2.30 ppm region, the dmpe ligand displays four distinct methyl groups. At elevated temperatures, these four methyl groups are averaged to two methyl groups with a coalesence temperature (310 K) close to those of the two phosphorus nuclei. Above 60 °C, the two averaged methyl resonances become broadened due to the decomposition of the cations, and the methyl resonances of free dmpe gradually appear as a doublet at δ 2.10 ppm. These NMR results imply that the fluxional process involves creation of a mirror plane bisecting the pentadienyl ligand, which in turn exchanges the ends of the bis(phosphino) ligand. The calculation of ΔG^* values based on variable-temperature ^{31}P NMR spectra leads to a value of 19.8 ± 0.3 kcal mol^{-1} for **2a** (in 1,2-$C_2D_4Cl_2$) and 15.2 ± 0.3 kcal mol^{-1} for **2b** (in 1,2-$C_2D_4Cl_2$).

Scheme II. Proposed Mechanism Involving Metal–Dienyl Bond Rotation



Scheme III. Basic Skeletal Rearrangement in a Pseudorotation-like Mechanism



A

Two possible mechanisms are compatible with our dynamic NMR data: (1) rotation of the metal–dienyl bond and (2) a pseudorotation-like mechanism involving a square pyramid–trigonal bipyramid interconversion. Mechanism 1 is a more common process for most asymmetric U-shaped pentadienyl complexes.[12,13] The pseudorotation-like mechanism has been established for $C_5H_5ML_4$ complexes, which has accounted for cis–trans isomerization of the related ion [CpMo$(CO)_2(PR_3)_2$]$^+$.[14] As depicted in Schemes II and III, these two processes could lead to averaging of the phosphorus atoms and two ends of the pentadienyl protons. Notably, the average form of the metal–η^5-dienyl rotation mechanism is expected to show two methyl groups (1 $\rightleftarrows$ 1′, 2 $\rightleftarrows$ 2′). A similar behavior is also expected in the pseudorotation-like mechanism in which the site exchanges 1 $\rightleftarrows$ 1′ and 2 $\rightleftarrows$ 2′ are operative. At the present stage, there is not sufficient data to differentiate between these two mechanisms.

Conclusions

The present studies have shown the feasibility of the $\eta^5 \rightleftarrows \eta^3$ interconversion for tungsten–pentadienyl complexes. For the η^3 − CH_3CN $\rightleftarrows$ η^5 + CH_3CN equilibrium, thermal parameters calculated from K_{eq} at various temnperatures produce ΔH = 8–11 kcal mol^{-1} and ΔS = 29–30 eu. These values reflect a delicate balance between these two species. Molecular structures and dynamic NMR studies of the tungsten–dienyl cation are presented.

Experimental Section

(A) General Procedures. All manipulations were carried out under argon atmosphere or by Schlenk techniques. Tetrahydrofuran and diethyl ether were dried over sodium/benzophenone and distilled before use. CH_2Cl_2 and $CHCl_3$ were dried over P_2O_5 and distilled. CH_3CN was dried over CaH_2. Bis(dimethylphosphino)ethane (dmpe), bis(diphenylphosphino)ethane (dppe), and tungsten carbonyl were obtained from Strem Chemicals and used without purification.

NMR spectra were measured on a Bruker AM-400 (^{1}H 400.1 MHz) or a JEOL FX-100 (^{31}P 40.25 MHz) spectrophotometer, by reference to tetramethylsilane and H_3PO_4, respectively. Microanalyses were performed by the microanalytic laboratory at National Taiwan University, Taipei, Taiwan.

(B) Synthesis of (η^3-C_5H_7)WBr$(CO)_2(CH_3CN)_2$ (1a). Tungsten hexacarbonyl (10.0 g, 28.4 mmol) was refluxed in 30 mL of CH_3CN

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under argon for 4 days, and 1-bromo-2,4-pentadiene (4.38 g, 30.2 mmol) was added at 23 °C. The solution was stirred for 6 h during which time the color gradually turned deep red. The solution was concentrated to 15 mL, and the orange solids were filtered and washed twice with 10-mL aliquots of THF. Further recrystallization from slow evaporation of a saturated CH_3CN solution produced red rod-shaped crystals (12.3 g, 26.7 mmol). ^{1}H NMR (400 MHz, CD_3CN): δ 1.37 (d, 1 H, H^1), 1.97 (s, 3 H, CH_3CN), 2.07 (s, 3 H, CH_3CN), 2.31 (t, 1 H, H^4), 2.79 (d, 1 H, H^2), 3.50 (m, 1 H, H^3), 5.04 (dd, 1 H, H^7), 5.27 (dd, 1 H, H^6), 6.43 (m, 1 H, H^5), $J_{13} = J_{34} = 10.3$ Hz, $J_{23} + 6.8$ Hz, $J_{45} = 10.5$ Hz, $J_{56} = 16.6$ Hz, $J_{57} = 10.4$ Hz. ^{13}C NMR (100 MHz, CD_3CN): δ 1.30 (CH_3CN), 44.3 (CH^1H^2), 65.7, 67.4 ($CH^3 + CH^4$), 113.8 (CH^6H^7), 139.9 (CH^5), 217.2, 219.5 (2W – CO). IR (Nujol): ν(CO) 1936 (s), 1849 (s) cm^{-1}; ν(C=C) 1615 (w) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_2BrWO_2$: C, 28.1; H, 2.77; N, 5.97. Found: C, 28.9; H, 2.84; N, 5.82.

(C) Synthesis of (η^3-C_5H_7)WBr(CO)$_2$(dppe) (1b). Dppe (1.04 g, 2.63 mmol) in 15 mL of THF was added dropwise to 1.21 g of **1a** (2.50 mmol) dissolved in 30 mL of THF. The solution was stirred for 1 h. After removal of solvent, the residue was chromatographed through a silica gel column by using dichloromethane as the eluting solvent. An orange band was developed, collected, and evaporated to dryness to afford an orange solid. Recrystallization from CH_2Cl_2/ether yielded red blocklike crystals (1.29 g, 1.65 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (dd, 1 H, H^1), 2.15, 2.40, 2.95, 3.10 (complex m, 4 H, CH_2–CH_2–PPh_2), 2.93 (t, 1 H, H^4), 3.26 (dd, 1 H, H^2), 3.47 (m, 1H, H^3), 5.04 (dd, 1 H, H^7), 5.22 (dd, 1 H, H^6), 6.36 (dt, 1 H, H^5), $J_{13} = 10.2$ Hz, $J_{23} = 7.0$ Hz, $J_{34} = J_{45} = 10.0$ Hz, $J_{56} = 16.2$ Hz, $J_{57} = 10.0$ Hz, $J_{1P} = 6.7$ Hz, $J_{2P} = 3.2$ Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.11 (d, CH_2–PPH_2, $J_{CP} = 28$ Hz), 27.98 (d, CH_2–PPh_2, $J_{CP} = 26$ Hz), 42.4 (CH^1H^2), 76.4, 79.5 ($CH^4 + CH^3$), 115.7 (CH^6H^7), 137.9 (CH^5), 128.4, 132.2, 134.2 (C_6H_5), 241.7 (d, CO, $J_{PC} = 40$ Hz), 216.1 (d, CO, $J_{PC} = 30$ Hz). ^{31}P NMR (40.2 MHz, $CDCl_3$): δ 29.0 (d, $J_{PP'} = 23$ Hz, $J_{WP} = 175$ Hz), 22.9 (d, $J_{PP'} = 23$ Hz, $J_{WP} = 180$ Hz). IR (Nujol): ν(CO) 1926 (s), 1838 (s) cm^{-1}; ν(C=C) 1609 (w) cm^{-1}. Anal. Calcd for $C_{33}H_{31}WO_2BrP_2$: C, 50.46; H, 3.95. Found: C, 49.97; H, 4.00.

(D) Synthesis of (η^3-C_5H_7)WBr(CO)$_2$(dmpe) (1c). This complex was prepared similarly from the reaction between (η^3-C_5H_7)W(CO)$_2$-(CH_3CN)$_2$Br and dmpe in tetrahydrofuran; the yield is 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65, 1.68, 1.72, 1.76 (d, d, d, d, 12H, PCH_3, $J_{PH} = 8.8$ Hz), 1.90 (m, 2 H, PCH_2), 1.98 (dd, 1 H, H^1), 2.00 (m, 2 H, PCH_2), 3.18 (dd, 1 H, H^2), 3.27 (t, 1 H, H^4), 4.55 (m, 1 H, H^3), 5.01 (dd, 1 H, H^7), 5.23 (dd, 1 H, H^6), 6.36 (m, 1 H, H^5), $J_{13} = 10.2$ Hz, $J_{23} = 6.8$ Hz, $J_{34} = J_{45} = 10.0$ Hz, $J_{56} = 16.0$ Hz, $J_{57} = 10.0$ Hz, $J_{1P} = 4.7$ Hz, $J_{2P} = 6.0$ Hz. ^{13}H NMR (100 MHz, $CDCl_3$): δ 12.8, 13.4, 15.8, 16.3 (d, d, d, d, P(CH_3)$_2$, $J_{PC} = 70$ Hz), 28.2, 28.7 (d, d, PCH_2, $J_{PC} = 52$ Hz), 47.2 (CH^1H^2), 73.2, 89.3 ($CH^3 + CH^4$), 114.3 (CH^6H^7), 138.8 (CH^5), 217.8 (d, CO, $J_{PC} = 40$ Hz), 218.8 (d, CO, $J_{PC} = 28$ Hz). ^{31}P NMR (40.2 MHz, $CDCl_3$): δ 13.6 (d, $J_{PP} = 23$ Hz, $J_{WP} = 200$ Hz), 12.2 (d, $J_{PP} = 23$ Hz, $J_{WP} = 190$ Hz). IR (Nujol): ν(CO): 1921 (s), 1826 (s) cm^{-1}; ν(C=C) 1608 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{23}WO_2BrP_2$: C, 29,06; H, 4.28. Found: C, 29.26; H, 4.12.

(E) Synthesis of [(η^5-C_5H_7)W(CO)$_2$(dppe)]PF_6 (2a). Complex **1b** (0.98 g, 1.25 mmol) was dissolved in 20 mL of CH_2Cl_2, and 0.33 g of $AgPF_6$ (1.30 mmol) was added. The resulting yellow solution was filtered and passed through a 5-cm silica column. Following removal of CH_2Cl_2, the resulting solid was crystallized from CH_2Cl_2/ether to give yellow blocklike crystals of **2a** (0.74 g, 0.88 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ –0.22 (m, 1 H, H^2), –0.01 (m, 1 H, H^6), 2.92 (dd, 1 H, H^2), 3.76 (d, 1 H, H^1), 3.86 (m, 1 H, H^5), 5.20 (m, 1 H, H^3), 6.17 (t, 1 H, H^4), $J_{13} = 7.5$ Hz, $J_{23} = 10.7$ Hz, $J_{34} = J_{45} = 6.9$ Hz, $J_{56} = 11.0$ Hz, $J_{57} = 7.4$ Hz, $J_{2P} = 3.4$ Hz, $J_{6P} = 3.8$ Hz, $J_{7P} = 2.8$ Hz. ^{13}C NMR (100 MHz, acetone-d_6: δ 29.7, 30.1 (d, d, CH_2P, $J_{PC} = 45$ Hz), 60.3, 67.3 ($CH^1H^2 + CH^6H^7$), 92.8, 96.3, 104.2 ($CH^3 + CH^4 + CH_5$); 129.3, 130.4, 130.7, 133.5 (C_6H_5), 217.1 (d, $J_{CP} = 40$ Hz), 217.9 (d, $J_{PC} = 30$ Hz). ^{31}P NMR (40.2 MHz, CD_3COCD_3): δ +48.3 (d, $J_{PP} = 14$ Hz, $J_{WP} = 210$ Hz), 39.3 (d, $J_{PP} = 14.6$ Hz, $J_{WP} = 220$ Hz). IR (CH_2Cl_2): ν(CO): 1985 (s), 1920 (s) cm^{-1}. Anal. Calcd for $C_{33}H_{31}WO_2F_6P_3$: C, 46.60; H, 3.65. Found: C, 46.47; H, 3.52.

(F) Synthesis of [(η^5-C_5H_7)W(CO)$_2$(dmpe)]PF_6 (2b). This complex was obtained similarly from the reaction between **1c** (1.00 g, 1.89 mmol) and $AgPF_6$ (0.48 g, 1.90 mmol) in 20 mL of CH_2Cl_2. Yellow crystals of **2b** (0.78 g, 1.30 mmol) were obtained after recrystallization from CH_2Cl_2/ether. ^{1}H NMR (400 MHz, acetone-d_6): δ 0.40–0.51 (complex m, 2 H, $H^6 + H^2$), 1.61, 1.73, 1.76, 2.04 (d, d, d, d, 12 H, $J_{PH} = 9.0$ Hz), 2.18, 2.38 (m, 4 H, P*CH*$_2$–*CH*$_2$′), 3.23 (m, 1 H, H^7), 3.44 (d, 1 H, H^1), 5.13–5.20 (complex m, 2 H, $H^3 + H^5$), 6.19 (t, 1 H, H^4), $J_{13} = 7.2$ Hz, $J_{23} = 10.4$ Hz, $J_{34} = J_{45} = 6.5$ Hz, $J_{57} = 7.2$ Hz, $J_{2P} = 3.5$ Hz, $J_{6P} = 5.5$ Hz, $J_{7P} = 3.0$ Hz. ^{31}P NMR (40.2 MHz, CD_3COCD_3): δ 40.8 (d, $J_{PP'} = 28.1$ Hz, $J_{WP} = 200$ Hz), 48.9 (d, $J_{PP'} = 28.1$ Hz, $J_{WP} = 210$ Hz). IR (CH_2Cl_2): ν(CO) 1982 (s), 1915 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{23}WO_2P_3F_6$: C, 25.92; H, 3.82. Found: C, 26.24; H, 3.92.

Table V. Summary of Crystal Data

empirical formula	$C_{13}H_{23}O_2P_2BrW$ (**1c**)	$C_{33}H_{31}O_2F_6P_3W$ (**2a**)
space group	orthorhombic; *Pbca*	triclinic; $P\bar{1}$
unit cell dimens		
a, Å	12.400 (5)	11.047 (4)
b, Å	13.226 (4)	11.457 (4)
c, Å	22.100 (6)	14.311 (5)
α, deg		86.08 (3)
β, deg		80.53 (3)
γ, deg		66.19 (3)
V, Å^3	3624 (2)	1634.5 (9)
Z	8	2
fw	537.0	850.3
ρ_{calc}, Mg/m^3	1.968	1.728
abs coeff, mm^{-1}	8.868	3.816
Mo Kα radiation: λ, Å	0.71071	0.71073
T, K	296	297
transm coeff	0.536/0.807	
final *R* indices (obs data)		
R, %	3.26	2.68
R_w, %	3.33	2.74

(G) Synthesis of [(η^3-C_5H_7)W(CO)$_2$(dppe)(CH_3CN)]PF_6 (3a). Method A. Complex **1b** (1.02 g, 1.30 mmol) was dissolved in 20 mL of CH_3CN, and 0.32 g of $AgPF_6$ (1.30 mmol) was added. The resulting yellow solution was filtered and passed through a 5-cm silica column. Following removal of CH_3CN, the resulting yellow solution was crystallized from CH_3CN/ether to give 0.98 g of yellow crystalline **3a** (1.1 mmol, 84%). ^{1}H NMR (400 MHz, CD_3CN): δ 2.16 (d, 1 H, H^1), 2.68–2.85 (m, 2 H, CH_2P), 2.90–3.05 (m, 2 H, PCH_2), 4.30 (m, 1 H, H^3), 5.23 (d, 1 H, H^7), 5.51 (d, 1 H, H^6), 6.24 (ddd, 1 H, H^5), 7.57–7.69 (complex m, 20 H, C_6H_5), $J_{13} = 10.6$ Hz, $J_{23} = 6.5$ Hz, $J_{34} = J_{45} = 10.2$ Hz, $J_{56} = 17.0$ Hz, $J_{57} = 10.8$ Hz, $J_{7P} = 7.6$ Hz. ^{31}P NMR (40.2 MHz, CD_3CN): δ 44.2 (d, $J_{PP} = 13.2$ Hz, $J_{WP} = 222$ Hz), 38.3 (d, $J_{PP'} = 13.2$ Hz, $J_{WP} = 210$ Hz). IR (CH_3CN): ν(CO) 1945 (s), 1865 (s) cm^{-1}; ν(C=C) 1608 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{34}WO_2P_3F_6N$: C, 47.15; H, 3.81; N, 1.57. Found: C, 47.00; H, 3.64; N, 1.66.

Method B. Complex **2a** (0.13 g, 0.15 mmol) was dissolved in 20 mL of CH_3CN and stirred for 1 h. The solution was evaporated to dryness, and the residues were recrystallized from CH_3CN/ether to give 0.109 g of yellow crystals of **3a** (0.12 mmol, 80%).

(H) Synthesis of [(η^3-C_5H_7)W(CO)$_2$(dmpe)(CH_3CN)]PF_6 (3b). This complex was obtained similarly from the reaction between **1c** (1.00 g, 1.89 mmol) and $AgPF_6$ (0.48 g, 1.90 mmol) in CH_3CN. Yellow crystals of **3b** (0.78 g, 1.40 mmol) were obtained after recrystallization from CH_3CN/ether. ^{1}H NMR (400 MHz, CD_3CN): δ 1.66, 1.72, 1.82, 1.90 (d, d, d, d, P–CH_3, 12 H), 2.00 (s, 3 H, CD_3CN), 2.17 (dd, 1 H, H^1), 3.43 (t, 1 H, H^4), 3.60 (dd, 1 H, H^2), 4.65 (m, 1 H, H^3), 5.19 (d, 1 H, H^7), 5.41 (d, 1 H, H^6), 6.31 (d, 1 H, H^5), $J_{13} = 10.2$ Hz, $J_{23} = 6.9$ Hz, $J_{34} = 10.3$ Hz, $J_{45} = 10.3$ Hz, $J_{56} = 17.0$ Hz, $J_{57} = 10.2$ Hz, $J_{1P} = 4.5$ Hz, $J_{2P} = 5.4$ Hz. ^{31}P NMR (40.2 MHz, CD_3CN): δ 24.2 (d, $J_{PP'} = 24.4$ Hz, $J_{PW} = 200$ Hz), 21.6 (d, $J_{PP'} = 25$ Hz, $J_{PW} = 205$ Hz). IR (CH_3CN): ν(CO) 1944 (s), 1854 (s) cm^{-1}; ν(C=C) 1606 cm^{-1}. Anal. Calcd for $C_{15}H_{26}WNO_2P_3F_6$: C, 28.01; H, 4.08; N, 2.18. Found: C, 32.55; H, 4.78; N, 2.64.

(I) X-ray Diffraction Study of 1c and 2a. Single crystals of **1c** and **2a** used for X-ray diffraction study were grown from a saturated CH_2Cl_2/diethyl ether solution cooled at –20 °C. Data were collected at room temperature on a Nicolet R3m/V diffractometer, using graphite-monochromated Mo Kα radiation. Crystal data and details of data collection, and structural analysis are summarized in Table V.

The structures of **1c** and **2a** were solved by direct methods using SHELXTL PLUS program. All atoms other than hydrogens were located on *E* maps and refined with anisotropic thermal parameters. Hydrogens which were included in the structure factor calculations were placed at their calculated positions and refined with fixed temperature factors.

(J) Dynamic NMR Studies. Samples were prepared in 1,2-$C_2D_4Cl_2$, and NMR spectra were recorded over the temperature range –60 to +120 °C. Probe temperatures were calibrated by using the temperature dependence of the differences in chemical shifts between the ^{1}H resonances of the methyl and hydroxyl groups of methanol below ambient temperatures and between the ^{1}H resonances of the methylene and hydroxyl groups of ethylene glycol above ambient temperatures.

The rate constants k_c at the coalescence temperature were calculated according to the formula[17]

$$k_c = \pi(\Delta\nu)/2$$

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[17] Johnson, C. S. *Am. J. Phys.* **1967**, *35*, 928.

in which $\Delta\nu$ is the difference in frequency between the two exchanging sites in the stopped-exchange limit. These rate constants were used to determine the Gibbs energy of activation $\Delta G^{\ddagger}$ at the coalescence temperature T_c from the Erying equation

$$k_c = (k_b/\hbar)T_c e^{-\Delta G^{\ddagger}/RT_c}$$

in which k_b = Boltzmann constant, $\hbar$ = Planck's constant/2π, and R = ideal gas constant.

(K) Equilibrium Constants and ΔH and ΔS Measurements. The positions of equilibrium **2a** ⇄ **3a** and **2b** ⇄ **3b** were determined from ^{31}P NMR spectra. Samples of **3a** and **3b** were weighed and dissolved in a known volume of CD_3COCD_3. The concentrations of the solutions were ca. $(0.1–2.0) \times 10^{-3}$ M. In the case of equilibrium between **2b** and **3b**, added CH_3CN was present in concentration in the range $(0.20–4.0) \times 10^{-3}$ M. In measurement of thermal parameters ΔH and ΔS, equilibrium constants K_{eq} were measured in the temperature ranges −10 to +20 °C. The probe temperatures were calibrated as described in section J of the Experimental Section. The errors of ΔH and ΔS are reported as the standard deviation from the mean value of three independent runs.

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Supplementary Material Available: Plots of ln K_{eq} versus $1/T$ and their numerical values (**3a** ⇄ **2a**; **3b** ⇄ **2b**) and, for **1c** and **2a**, tables giving final coordinates, bond distances, angles, anisotropic displacement parameters for non-hydrogen atoms, and crystal data (11 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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NMR Study of the Chemical Exchange of the Hydrido Ligands in the Bis(bis(diphenylphosphino)ethane)trihydridodiplatinum(II) Cation by T_1, T_2, and HD Isotopic Perturbation

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Proton longitudinal and transverse relaxation rates of hydrido resonances of different isotopomers in $[H_3Pt_2(Dpe)_2][BF_4]$ [Dpe = bis(diphenylphosphino)ethane] show significant differences in the satellite peaks with respect to the central ones that can be used to evaluate the activation energy of the intramolecular exchange process and the chemical shift separation between bridging and terminal sites. An alternative route to get an estimation of the chemical shift values of the bridging and terminal hydrides in this derivative has been pursued by considering the isotopic shift of the three H_3, H_2D, and HD_2 isotopomers at different temperatures.

$[H_3Pt_2(Dpe)_2]^+[BF_4]^-$ [Dpe = bis(diphenylphosphino)ethane] contains five- and four-coordinated Pt atoms linked through two bridging H atoms and has been described as a donor–acceptor complex in which a neutral 16-electron H_2Pt(diphosphine) unit acts as a donor to a cationic 14-electron $[HPt(\text{diphosphine})]^+$ unit.

Neutron diffraction analysis[1] (Figure 1) was performed to directly locate the hydride ligands showing the presence of a marked asymmetry in the μ_2-bridging hydrides. Variable-temperature ^1H NMR studies[2b] were consistent with a rapid exchange of the terminal and bridging hydride ligands, which cannot be "frozen out" down to the lowest accessible temperature.

The use of proton longitudinal relaxation times as structural probes for hydrido ligands has already been reported.[3] Accurate H–H distances can be obtained in polynuclear cluster compounds as well high relaxation rates can support the presence of nonclassical H_2 ligands in mononuclear systems.[4]

Results and Discussion

In the title compound the hydride region shows a pattern of quintets of quintets resulting from the coupling of the hydride resonance with four equivalent phosphorus (^{31}P, $I = 1/2$, natural abundance 100%) and two equivalent Pt nuclei (^{195}Pt, $I = 1/2$, natural abundance 33.8%). The analysis of this spectral pattern provides averaged values for proton–phosphorus and proton–platinum coupling constants (Figure 2).

Table I reports the values for T_1 and T_2 for central and satellite peaks as measured at different temperatures in CD_2Cl_2 solution. The presence of different isotopomers and the fast chemical exchange cause significant differences in the longitudinal and transverse relaxation rates of the satellite peaks with respect to the central ones.

Table I. Spin–Lattice and Spin–Spin Relaxation Times of $[H_3Pt_2(Dpe)_2]^+[BF_4]^-$ for Central and Satellite Peaks at Different Temperatures in CD_2Cl_2 Solution

	temp, °C							
	22	0	−15	−32	−50	−65	−82	−91
			T_1 (ms)					
central peaks	1162	876	698	542	428	439	630	776
satellite peaks	989	785	644	454	331	346	445	555
			T_2 (ms)					
central peaks	1030	807	589	437	218	143	55	45
satellite peaks	847	675	474	335	173	119	44	32

Central Peaks. The T_1 of these resonances is determined mainly by H–H and P–H dipolar interactions modulated by the molecular tumbling; other contributions (chemical shift anisotropy, CSA, and spin rotation, SR) may be present, but they are expected to contribute much less to the overall relaxation rate of the hydride resonances.

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