6p orbitals[23] with the levels calculated for cyclopentadiene[20,24] suggests that hyperconjugation should favor a high contribution of the 6p orbital in the Pt–Cp bond. This means that it would have more 6p character (less 6s) than the Pt–CH_3 bond. Thus the presence of hyperconjugation in **1** would lead to the prediction that the Pt–Cp bond would be longer and have a weaker NMR and structural trans influence than the Pt–CH_3 bond, as was observed. Hyperconjugation is not possible for **2**, where the diene no longer exists; thus the close similarity of the NMR trans influences observed for the two sp^3-carbon ligands is expected.

Ultraviolet data for substituted cyclopentadienes have been analyzed and used as a criterion to predict the presence or absence of σ–π hyperconjugation.[22a] The value of the lowest band ($\pi_2 \rightarrow \pi_{3*}$) is low (4.0 eV) for molecules such as $C_5Cl_4(OCH_3)_2$ where hyperconjugation is not expected due to the electronegativity of the substituent. The same band in the spectrum of **1** appears at 4.8 eV, very close to the values for C_5H_5 (4.8 eV) and $C_5H_5SiMe_3$ (5.1 eV) for which hyperconjugation is thought to be important. Thus the ultraviolet spectrum of **1** is also consistent with the postulate of hyperconjugation.

The spectroscopic and structural features of **1** are consistent with the postulate that steric and hyperconjugative effects cause the Pt–Cp bond to be quite different from Pt–CH_3 bond. The consistency of these features with hyperconjugation is particularly noteworthy. The latter phenomenon has been correlated[21] with the ease of fluxional[25] behavior and other ground-state parameters of group 4A cyclopentadienyl complexes. The Cp ring in **1** is nonrigid and exhibits a sharp line in its ^1H NMR spectrum even at −90 °C.[2] Thus, the barrier to rearrangement in transition-metal η^1-Cp complexes may also be directly related to the degree of σ–π hyperconjugation of the M–Cp bond.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (V.W.D.), for support of this work.

Registry No. 1, 56200-09-0.

Supplementary Material Available: Listing of structure amplitudes (12 pages). Ordering information is given on any current masthead page.

---

(22) (a) G. Wulfsberg, R. West, and V. N. M. Rao, *J. Am. Chem. Soc.*, **95**, 8658 (1973). (b) G. Wulfsberg, *J. Organomet. Chem.*, **86**, 321 (1975).

(23) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

(24) A. Streitwieser in "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.

(25) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968).

Contribution from the Department of Chemistry, University of Western Ontario,
London, Ontario, Canada N6A 5B7

Structure of the Diels–Alder Product from Reaction of Hexafluoro-2-butyne with the η^1-C_5H_5 Ring in (1,5-Cyclooctadiene)(η^1-cyclopentadienyl)methylplatinum(II)

DAVID G. IBBOTT, NICHOLAS C. PAYNE,* and ALAN SHAVER*[1]

Received December 9, 1980

A three-dimensional X-ray structure analysis has shown that the Diels–Alder ($2\pi + 4\pi$) addition of $CF_3C{\equiv}CCF_3$ to the η^1-C_5H_5 ring in Pt(COD)(η^1-C_5H_5)(CH_3) (**1**), where COD = 1,5-C_8H_{12}, occurs from the side opposite the platinum atom to give the norbornadiene derivative Pt(COD)(7-η-$C_9F_6H_5$)(CH_3) (**2**). Crystals are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions a = 23.606 (5) Å, b = 8.361 (3) Å, c = 8.936 (2) Å, and β = 93.30 (1)°. Full-matrix least-squares refinement on F converged at R = 0.072. The molecule is a square-planar Pt(II) complex with equal Pt–C(sp^3) distances: Pt–CH_3, 2.054 (14) Å; Pt–C(7), 2.054 (10) Å. The Pt–olefin distances are very similar. This is consistent with the similarity of the NMR trans influences previously found for the two carbon sp^3 ligands in **2**.

Introduction

Cycloaddition reactions between electrophiles and transition-metal-coordinated polyolefins have been known for some time.[2-10] Of the many examples of this class of reaction, the recent applications to the synthesis of natural product derivatives[11] are among the most interesting. It is clear that these sophisticated schemes are based[12] upon a great many investigations of simpler systems. The metal can play any one or more of a number of crucial roles by: (a) lifting symmetry constraints thus permitting symmetry forbidden thermal cycloadditions, (b) producing a template effect via coordination

---

(1) Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada H3A 2K6.

(2) (a) H. Gilman and L. A. Gist, Jr., *J. Org. Chem.*, **22**, 250 (1957); (b) C. S. Kraihanzel and M. L. Losee, *J. Am. Chem. Soc.*, **90**, 4701 (1968).

(3) A. R. L. Bursics, M. Munay, and F. G. A. Stone, *J. Organomet. Chem.*, **111**, 31 (1976), and references therein.

(4) (a) D. W. McBride, E. Dukek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964); (b) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 714 (1963); (c) D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 497 (1962).

(5) (a) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *J. Am. Chem. Soc.*, **94**, 8251 (1972); (b) A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *ibid.*, **98**, 3495 (1976); (c) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

(6) J. L. Davison, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 286 (1975); *J.. Chem. Soc., Dalton Trans.*, 2044 (1976).

(7) J. P. Williams and A. Wojcicki, *Inorg. Chem.*, **16**, 3116 (1977).

(8) (a) M. Bottrill, R. Goddard, M. Green, R. P. Hughes, M. K. Lloyd, B. Lewis, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 253 (1975); (b) R. Davis, M. Green, and R. P. Hughes, *ibid.*, 405 (1975).

(9) (a) J. S. Ward and R. Pettit, *J. Am. Chem. Soc.*, **93**, 262 (1971); (b) R. E. Davis, T. A. Dodds, T.-H. Hseu, J. C. Wagnon, T. Devon, J. Tancrede, J. S. McKennis, and R. Pettit, *ibid.*, **96**, 7562 (1974).

(10) (a) J. A. Evans, R. D. W. Kemmitt, B. Y. Kimura, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 509 (1972); (b) A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *ibid.*, 797 (1974).

(11) R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 5483 (1977); **101**, 215 (1979).

(12) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).

0020-1669/81/1320-2193$01.25/0

which may overcome large negative entropy factors, and (c) activating by coordination to electrophilic metal species. One of the earliest and simplest systems is the ($2\pi + 4\pi$), Diels–Alder-type addition of electrophilic acetylenes to coordinated cyclopentadienyl groups.[2-7] η^1-Cyclopentadienyl compounds of silicon and tin add to acetylenes to give norbornadienes substituted in the apical or 7 position.[2] It is generally assumed that the acetylene approached and added to the ring on the side opposite the metal to produce only the anti isomer. Thus, the steric bulk of the organometallic substituent on the C_5H_5 ring is thought to dominate and prevent attack on the same side. A similar and reasonable assumption has been applied to the assignment of similar derivatives involving mercury.[3]

Transition metals, however, can bond to acetylenes and activate them as dieneophiles. Thus, the assumptions about geometry applied to non-transition-metal η^1-C_5H_5 complexes are not valid since precoordination might give rise to the syn isomer with the metal performing the dual role of activator and template. One of the first cycloadditions of this type reported for a transition-metal complex was the addition of acetylenes to nickelocene.[4] X-ray analysis[4b] of the product made it clear that addition had occurred from the same side of the ring as the nickel atom such that the double bond of the norbornadiene formed by the acetylene was bonded to the metal atom. These and other reactions led to an appreciation of the reactivity of nickelocene, and to the postulate[13] that an intermediate containing a coordinated acetylene and a η^1-C_5H_5 ring was involved. This has provided a model of metal participation for this type of cycloaddition.

However, the geometry of addition found for nickelocene may not be generally applicable to other transition-metal complexes. The assignment is not simple in most cases. Although the position of the metal on C_7 of the norbornadiene ring can be readily assigned by ^{1}H NMR, the syn/anti assignment can rarely be made with any certainty. The complex (η^5-C_5H_5)Fe(CO)$_2$(7-η-$C_9F_6H_5$), the Diels–Alder product of $CF_3C{\equiv}CCF_3$ and (η^5-C_5H_5)(η^1-C_5H_5)Fe(CO)$_2$, has been assigned in one case the syn[6] geometry and in another the anti.[7]

When the complex Pt(COD)(η^1-C_5H_5)(CH_3) (**1**), where COD = 1,5-cyclooctadiene, was treated with $CF_3C{\equiv}CCF_3$ and maleic anhydride, it was relatively easy to deduce the presence of a $2\pi + 4\pi$ type addition product, but the question of the geometry at C_7 arose. Unlike some previous systems, **1** is a 16-electron complex; thus precoordination of the acetylene does not require preliminary ligand dissociation. Syn and anti addition both seemed to be reasonable alternatives. An X-ray analysis was undertaken, and the results, reported in full here, indicate that addition occurred on the side opposite the platinum atom to give the anti isomer Pt(COD)(7-η-$C_9F_6H_5$)(CH_3) (**2**). A communication of this finding has appeared.[14]

The structural details of **2** have importance with respect to the discovery that hyperconjugation plays a role in determining the bond lengths in the inner coordination sphere of **1**. This phenomenon, described in detail in a previous paper,[15] results in the trans influence (both NMR and structural) of the η^1-C_5H_5 group being noticeably smaller than that of the methyl group. However, hyperconjugation is not possible for **2** since the diene of the Cp group has been eliminated by the Diels–Alder reaction. The NMR trans influence of the norbornadiene ligand is the same as the methyl ligand, as expected.[16] Since the effects observed for **1** might have been due to steric effects it became important to examine the bond lengths in **2** for which the steric factors should be very similar. Finally, these structural determinations present an interesting study of the simple chemical conversion of the starting material **1** to the product **2**.

Table I. Crystal Data and Experimental Conditions

$C_{18}H_{20}F_6Pt$	fw 545.44
$a = 23.606$ (5) Å	space group $P2_1/n$, $Z = 4$
$b = 8.361$ (3) Å	d(obsd) = 2.01 (1) g cm^{-3}
$c = 8.936$ (2) Å	d(calcd) = 2.064 g cm^{-3}
$\beta = 93.30$ (1)°	
radiation	Cu Kα, λ(Kα_1) = 1.540 51 Å
receiving aperture	5.0 × 5.0 mm^2, 32 cm from crystal
scan	θ–2θ, at 2° min^{-1}
background	stationary crystal and counter, 10 s at scan limits
index limits	h, 0 to 27; k, −10 to 0; l, −10 to 10

Experimental Section

The synthesis and spectroscopic properties of **2** have been described elsewhere.[16] Since our first report, intensity data have been recollected from crystals of (1,5-cyclooctadiene)(*anti*-7-η-5,6-bis(trifluoromethyl)(bicyclo[2.2.1]hepta-2,5-dienyl))methylplatinum(II), Pt(COD)(7-η-$C_9F_6H_5$)(CH_3) (**2**). Colorless crystals of **2** were recrystallized from diethyl ether at −20 °C and sealed in glass capillary tubes. A photographic study with use of Weissenberg and precession cameras suggested monoclinic symmetry, and preliminary cell dimensions were measured. Systematic absences of k odd for $0k0$ and $h + l$ odd for $h0l$ are consistent only with space group $P2_1/n$, $\pm(x, y, z)$, $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$, an alternative setting of $P2_1/c$—No. 14.[17] The density was measured by flotation in a mixture of 1,2-dibromoethane and carbon tetrachloride; there are four molecules per cell, and no imposed symmetry.

Collection and Reduction of X-ray Data. The crystals are sensitive to X-ray damage, and three different data sets were recorded on a Picker FACS-1 diffractometer before an acceptable refinement was obtained. The third crystal was of approximate dimensions 0.43 × 0.28 × 0.11 mm, elongated along [010], with ten faces $\{100\}$, $\{101\}$, $\{10\bar{1}\}$, (010), $(1\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$, and $(20\bar{1})$. Twenty-two strong reflections with $40 < 2\theta < 61°$ were carefully centered at 20 °C, and cell constants and an orientation matrix were calculated from the angular settings. ω scans of several intense, low-angle reflections were symmetrical, with an average width of 0.09° at half-height. Though this is acceptable,[18] at the conclusion of data collection all had broadened noticeably, to an average width of 0.14°. Five standard reflections, $0\bar{2}0$, $00\bar{2}$, 400, $2\bar{1}1$, and 002, were monitored every 200 data recorded but showed only random fluctuations.

Intensity data were recorded in three shells out to a maximum 2θ value of 130°. The deterioration of the crystal lattice required that the scan width be steadily widened, from the starting value of 1.4°, corrected for dispersion, to a maximum of 2.2°. Over a period of 114 h, 3134 reflections were measured, of which 75 were standards. Crystal data and experimental conditions are summarized in Table I.

The data were corrected for background and Lorentz–polarization effects and standard deviations assigned.[19] An absorption correction was applied to all reflections with $I > 0$ with use of the analytical method of de Meulenaer and Tompa;[20] transmission factors varied from 0.04 to 0.26. For solution and preliminary refinement of the structure, the 2563 unique data with $F^2 > 3\sigma(F^2)$ were used.

Structure Solution and Refinement. The Pt atom was found from a Patterson synthesis and the other 24 nonhydrogen atoms from a

---

(13) K. W. Barnett, *J. Organomet. Chem.*, **78**, 139 (1974).

(14) H. C. Clark, D. G. Ibbott, N. C. Payne, and A. Shaver, *J. Am. Chem. Soc.*, **97**, 3555 (1975).

(15) C. S. Day, V. W. Day, A. Shaver, and H. C. Clark, *Inorg. Chem.*, previous paper in this issue.

(16) H. C. Clark and A. Shaver, *Can. J. Chem.*, **54**, 2068 (1976).

(17) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England, 1974: (a) Vol. I; (b) Vol. IV.

(18) T. C. Furnas, "Single Crystal Orienter Manual", General Electric Co., Milwaukee, WI, 1957.

(19) J. F. Richardson and N. C. Payne, *Inorg. Chem.*, **17**, 2111 (1978).

(20) The computer programs used include local modifications of the following: cell refinement and orientation matrix, PICKTT; full-matrix least squares, NUCLS, by J. A. Ibers; Fourier syntheses, FORDAP, by A Zalkin; molecular illustrations, ORTEP, by C. K. Johnson; functions and errors, ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy; absorption correction, AGNOST, by D. Cahen and J. A. Ibers.

Table II. Atomic Positional (×10^4) and Thermal (×10^3) Parameters[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	1152.5 (2)	−188.1 (5)	−2184.8 (5)	57.5 (4)	49.4 (3)	41.5 (3)	−1.5 (2)	−0.8 (2)	2.2 (2)
F(1)	1223 (5)	−6054 (13)	2459 (14)	143 (9)	73 (7)	198 (12)	0 (6)	−19 (9)	38 (7)
F(2)	481 (6)	−5660 (15)	1230 (14)	179 (12)	124 (8)	140 (10)	−96 (9)	−56 (9)	61 (8)
F(3)	600 (8)	−4828 (12)	3441 (16)	254 (17)	107 (9)	127 (10)	−50 (8)	90 (11)	10 (6)
F(4)	1820 (6)	−3847 (24)	4300 (17)	181 (13)	303 (20)	163 (12)	−109 (14)	−103 (11)	166 (14)
F(5)	2365 (7)	−3533 (34)	2861 (13)	157 (12)	518 (32)	92 (8)	220 (18)	−40 (8)	−30 (14)
F(6)	2109 (8)	−1761 (17)	3998 (20)	311 (21)	133 (11)	253 (18)	30 (13)	−232 (18)	−22 (12)
C(8)	584 (7)	−1827 (18)	−3096 (14)	98 (11)	79 (9)	52 (7)	−12 (8)	−13 (7)	8 (6)
C(7)	1267 (5)	−1721 (13)	−397 (11)	47 (6)	53 (6)	43 (6)	−1 (5)	−1 (5)	1 (4)
C(1)	746 (5)	−2461 (14)	366 (12)	54 (7)	56 (7)	51 (6)	−8 (5)	−8 (5)	10 (5)
C(2)	525 (6)	−993 (18)	1163 (15)	60 (8)	77 (9)	73 (8)	16 (7)	11 (7)	26 (7)
C(3)	962 (7)	−181 (14)	1622 (14)	101 (11)	59 (8)	43 (6)	15 (7)	12 (7)	4 (5)
C(4)	1500 (5)	−1047 (14)	1179 (12)	67 (8)	55 (7)	49 (6)	−1 (6)	−11 (6)	9 (5)
C(5)	1507 (5)	−2603 (14)	2094 (11)	65 (8)	58 (7)	42 (5)	14 (6)	2 (5)	12 (5)
C(6)	1057 (5)	−3443 (14)	1628 (13)	67 (8)	47 (6)	56 (7)	−8 (6)	−3 (6)	12 (5)
C(9)	825 (8)	−4970 (15)	2159 (15)	106 (12)	60 (8)	51 (7)	−6 (8)	6 (7)	20 (6)
C(10)	1943 (7)	−2948 (19)	3261 (18)	80 (11)	74 (10)	80 (10)	9 (8)	−25 (8)	13 (8)
C(11)	1575 (7)	2022 (16)	−1146 (15)	98 (11)	56 (8)	63 (8)	−10 (7)	0 (8)	4 (6)
C(12)	1979 (6)	1092 (18)	−1705 (16)	70 (9)	76 (10)	79 (9)	−17 (8)	−16 (7)	19 (7)
C(13)	2225 (7)	1251 (23)	−3221 (18)	102 (12)	114 (14)	80 (10)	−7 (10)	28 (9)	17 (9)
C(14)	1810 (8)	1736 (22)	−4501 (16)	123 (14)	118 (14)	61 (8)	−6 (11)	29 (9)	25 (9)
C(15)	1240 (7)	1034 (19)	−4405 (14)	112 (12)	79 (10)	47 (7)	−14 (9)	13 (7)	16 (6)
C(16)	797 (7)	1723 (18)	−3758 (16)	99 (12)	70 (9)	64 (8)	2 (8)	−17 (8)	29 (7)
C(17)	817 (7)	3260 (20)	−2894 (21)	104 (13)	73 (11)	123 (14)	18 (9)	11 (11)	28 (10)
C(18)	1354 (8)	3521 (17)	−1884 (17)	151 (16)	55 (9)	77 (9)	−11 (9)	13 (10)	1 (7)

[a] $U_{ij} = \beta_{ij}/2\pi^2(a_i{}^*a_j{}^*)$ (in Å^2). The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits.

difference Fourier synthesis phased by its position. Atomic parameters were refined by full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, and the weight w is defined at $4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors for neutral atoms were taken from ref 17b; those for H were from Stewart et al.,[21] while anomalous scattering contributions were included for Pt and F as calculated by Cromer and Liberman.[22] Two cycles of refinement with anisotropic thermal parameters gave agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.111$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2} = 0.129$. Correction for absorption reduced R_1 to 0.071 and R_2 to 0.084. In a difference Fourier synthesis, 19 of the 20 H atoms were clearly visible, with densities ranging from 0.45 to 0.85 e Å^{-3}. All were included in idealized positions (sp^2/sp^3, C–H = 0.95 Å) with isotropic thermal parameters 10% greater than those of the atoms to which they are bonded. Several cycles of refinement, with recalculated H atom parameters, with use of 2878 unique data with $F^2 > \sigma(F^2)$ and 226 variables, converged at values of $R_1 = 0.072$ and $R_2 = 0.076$. A total difference Fourier synthesis contained eight peaks with densitites between 1.0 and 2.2 (3) e Å^{-3}, each with y close to 0.0 and approximately 1.5 Å from the Pt atom. We attribute these to errors caused by the crystal decomposition; none of these nor the next 20 peaks were of any chemical significance. In the final cycle all shifts were less than 0.1 σ, and the error on an observation of unit weight was 3.1 electrons. A statistical analysis of R_2 in terms of $|F_o|$, indices and diffractometer setting angles χ and ϕ showed no unusual trends, and there was no evidence for extinction. Agreement between chemically equivalent dimensions was good, and the atomic parameters reported in Table II represent the best we have been able to obtain from these crystals. H atom parameters are given in Table III, while structure amplitudes, as $10|F_o|$ vs. $10|F_c|$ in electrons, have been deposited.[23]

Table III. Hydrogen Atom Parameters

atom	x[b]	y	z	B, Å^2
H1C(8)[a]	266	−1888	−2484	6.77
H2C(8)	463	−1505	−4078	6.77
H3C(8)	762	−2848	−3124	6.07
H1C(7)	1508	−2565	−679	4.16
H1C(1)	479	−3023	−275	4.71
H1C(2)	138	−746	1290	6.16
H1C(3)	953	796	2187	5.94
H1C(4)	1843	−440	1205	5.02
H1C(11)	1423	1709	−225	6.29
H1C(12)	2123	258	−1072	6.65
H1C(13)	2523	2009	−3141	8.46
H2C(13)	2383	224	−3458	8.46
H1C(14)	1781	2862	−4511	8.60
H2C(14)	1961	1388	−5427	8.60
H1C(15)	1173	9	−4849	6.87
H1C(16)	445	1196	−3859	6.88
H1C(17)	784	4120	−3586	8.74
H2C(17)	501	3271	−2276	8.74
H1C(18)	1640	3951	−2470	8.16
H2C(18)	1271	4269	−1117	8.16

[a] H1C(8), H2C(8), etc. are bonded to C(8). [b] Positional parameters × 10^4.

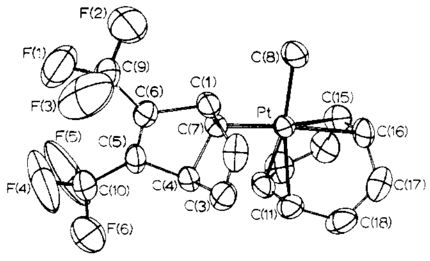


Figure 1. Atom numbering scheme used. Atoms are drawn as 40% probability thermal ellipsoids.

Results

The crystals are composed of discrete molecules; the shortest intermolecular distances of approach are 2.56 Å, between F(5) and H1C(4), and 2.57 Å, between H3C(8) and H1C(17). The atom numbering scheme is shown in Figure 1, with a stereoview given in Figure 2. Selected intramolecular dimensions are listed in Table IV. The molecule is best described as a square-planar platinum(II) complex with the syn olefin carbons being essentially nonbonding [Pt–C(2), 3.48 (1) and Pt–C(3), 3.46 (1) Å]. A weighted least-squares plane is described in Table V. The geometry of the substituted norbornadiene unit is clearly anti with respect to the platinum atom and the

---

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(22) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(23) Supplementary material.

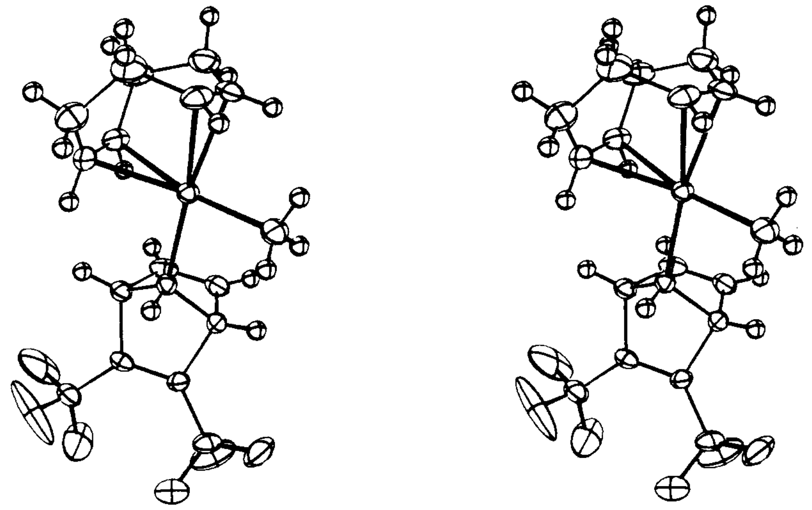


Figure 2. Stereoview of the molecule. Atoms other than H are drawn as 20% probability thermal ellipsoids.

Table IV. Selected Intramolecular Dimensions[a]

bond	dist, Å	bond	dist, Å
Pt-C(8)	2.054 (14)	C(7)-C(1)	1.57 (2)
Pt-C(7)	2.054 (10)	C(7)-C(4)	1.59 (1)
Pt- - -C(2)	3.479 (13)	C(1)-C(2)	1.53 (2)
Pt- - -C(3)	3.457 (12)	C(2)-C(3)	1.28 (2)
Pt-C(11)	2.273 (13)	C(3)-C(4)	1.53 (2)
Pt-C(12)	2.245 (13)	C(4)-C(5)	1.54 (1)
Pt-C(15)	2.252 (12)	C(5)-C(6)	1.32 (2)
Pt-C(16)	2.258 (12)	C(6)-C(1)	1.55 (1)
C(11)-C(12)	1.35 (2)	C(6)-C(9)	1.48 (2)
C(12)-C(13)	1.51 (2)	C(9)-F(1)	1.32 (2)
C(13)-C(14)	1.52 (2)	C(9)-F(2)	1.27 (2)
C(14)-C(15)	1.48 (2)	C(9)-F(3)	1.30 (2)
C(15)-C(16)	1.35 (2)	C(5)-C(10)	1.45 (2)
C(16)-C(17)	1.50 (2)	C(10)-F(4)	1.24 (2)
C(17)-C(18)	1.53 (2)	C(10)-F(5)	1.19 (2)
C(18)-C(11)	1.50 (2)	C(10)-F(6)	1.24 (2)
bonds	**angle, deg**	**bonds**	**angle, deg**
C(8)-Pt-C(7)	86.9 (5)	Pt-C(7)-C(1)	120.9 (7)
C(11)-Pt-C(12)	34.7 (5)	Pt-C(7)-C(4)	119.5 (7)
C(15)-Pt-C(16)	34.9 (5)	C(7)-C(1)-C(2)	100.6 (9)
C(8)-Pt-C(15)	92.5 (6)	C(7)-C(1)-C(6)	100.2 (9)
C(8)-Pt-C(16)	90.8 (6)	C(7)-C(4)-C(3)	98.4 (9)
C(7)-Pt-C(11)	98.9 (5)	C(7)-C(4)-C(5)	99.5 (9)
C(7)-Pt-C(12)	94.3 (5)	C(1)-C(2)-C(3)	106.5 (11)
		C(2)-C(3)-C(4)	109.3 (11)
C(11)-C(12)-C(13)	127 (1)	C(3)-C(4)-C(5)	104.2 (10)
C(12)-C(13)-C(14)	116 (1)	C(4)-C(5)-C(6)	107.4 (9)
C(13)-C(14)-C(15)	114 (1)	C(4)-C(5)-C(10)	122.4 (12)
C(14)-C(15)-C(16)	126 (2)	C(6)-C(5)-C(10)	130.2 (12)
C(15)-C(16)-C(17)	126 (2)	C(5)-C(6)-C(1)	106.7 (10)
C(16)-C(17)-C(18)	115 (1)	C(5)-C(6)-C(9)	131.6 (12)
C(17)-C(18)-C(11)	113 (1)	C(1)-C(6)-C(9)	121.7 (11)
C(18)-C(11)-C(12)	124 (1)		

[a] Weighted mean values: C-F, 1.259 (7) Å; C-F-F, 114.6 (5)°; F-C-F, 103.6 (6)°.

Table V. Weighted Least-Squares Planes

Pt Inner Coordination Sphere			
$17.56x - 4.101y - 4.429z = 3.069$			
Pt	0.0001 (5)[a]	C(11)	−0.62 (2)
C(8)	0.08 (2)	C(12)	0.71 (2)
C(7)	0.04 (1)	C(15)	0.64 (2)
		C(16)	−0.71 (2)
Cyclooctadiene Ring			
$9.663x + 7.008y - 3.427z = 3.726$			
C(11)	−0.39 (1)	C(15)	−0.29 (1)
C(12)	−0.46 (1)	C(16)	−0.46 (1)
C(13)	0.40 (2)	C(17)	0.34 (2)
C(14)	0.78 (2)	C(18)	0.69 (1)

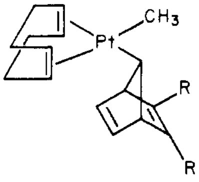
[a] Distances from the planes are given in Å.

trifluoromethyl groups. The platinum–carbon (sp^3) distances are the same [Pt–CH_3, 2.054 (14); Pt–C(7), 2.054 (10) Å] as are the platinum–carbon (olefin) mean distances [Pt–C(11), C(12), 2.259 (13) and Pt–C(15), C(16), 2.255 (12) Å]. This results in the platinum coordination sphere being more regular in **2** than in its precursor **1**.

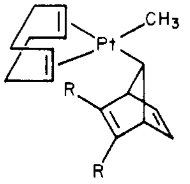
The cyclooctadiene ligand is twisted (Table V) in a similar fashion to that observed previously.[15] Bond distances and bond angles are internally consistent in the ligand and also with those in the precursor. Dimensions within the norbornadiene fragment are unexceptional. The CF_3 groups show considerable thermal motion; weighted mean dimensions for these are given in Table IV.

Discussion

There are two basic geometries (**2a,b**) possible for the



2a



2b

complex. That obtained was identified as **2a** by the single crystal X-ray structure determination. This geometry results from addition of C_4F_6 to the η^1-C_5H_5 ring on the side opposite the platinum atom and implies no direct metal atom participation, through either a template effect or activation of the acetylene via precoordination.

It seems reasonable to conclude that the metal species sterically hinders the ring on one side, directing the attack by the acetylene exclusively anti to it. It is possible, in view of the hyperconjugation of the Pt–Cp bond with the diene observed in the starting material, **1**, that the metal might have an electronic effect on the cycloaddition. However, this should not have stereochemical consequences. Kinetic studies are necessary to test for this type of metal substituent effect.

This result is important with respect to other systems where the geometry of addition has been based upon the similarity of the NMR data to that reported for the nickelocene examples where syn addition of acetylenes occurs. Such comparisons were ambiguous since there were no well-characterized examples of anti addition prior to **2** and others of its type.[16] The NMR data for **2** could have easily lead to the wrong assignment. It seems reasonable to conclude that the normal mode of attack by electrophilic acetylenes on η^1-C_5H_5 rings in stable metal complexes will be such as to afford the anti product, at least where other bulky ligands are coordinated to the metal.

The structure of **2** provides major confirmation of the postulate[15] of hyperconjugation in **1** whereby the electrons of the Pt–Cp bond are delocalized with those of the diene unit. This causes the Pt–Cp bond distance to be longer than the Pt–CH_3 one. Since such delocalization is not possible for **2**, the differences observed in the NMR and structural trans influences between the methyl and Cp groups of **1** should not be observed for the methyl and norbornadiene groups of **2**. This is indeed the case, for the bond distances of these latter ligands to platinum are the same in **2**. This was also evident in the ^{1}H NMR of **2**, where, although different resonances for the vinyl protons trans to the two ligands were resolved, the *J*(PtH(vinyl)) coupling constants were identical.[16] Comparing the two structures, the Pt–CH_3 distances in **1** and **2** are indistinguishable [**1**, 2.068 (8) and **2**, 2.054 (14) Å; 0.9σ] whereas the other Pt–C(sp^3) distances are quite different [Pt–Cp, 2.151 (8) and Pt–$C_7F_6H_5$, 2.054 (10) Å; 7.6σ]. Finally, the COD ligand in **2** is twisted in a manner similar to that in **1**, further substantiating the claim that the differences in the platinum–carbon(sp^3) bonds in **1** are not due to steric effects. This comparison of **1** and **2** is satisfyingly consistent with the postulate of hyperconjugative effects in **1**.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this work.

Registry No. **1**, 56200-09-0; **2**, 56200-13-6; $CF_3C{\equiv}CCF_3$, 692-50-2.

Supplementary Material Available: Listing of structure amplitudes (8 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Structural Studies on Some (η^5-C_5H_5)M(CO)$_3$X Molecules: (η^5-C_5H_5)W(CO)$_3$Cl, (η^5-C_5H_5)Mo(CO)$_3$Cl, and (η^5-C_5H_5)Mo(CO)$_3$HgCl

CLIFFORD BUENO and MELVYN ROWEN CHURCHILL*

Received December 10, 1980

Single-crystal X-ray diffraction studies have been completed on three simple (η^5-C_5H_5)M(CO)$_3$X derivatives. Crystal data are as follows: for (η^5-C_5H_5)W(CO)$_3$Cl, $P2_1/n$, a = 7.9732 (19) Å, b = 10.695 (6) Å, c = 11.3719 (18) Å, β = 99.096 (16)°, R_F = 3.3% for 1690 reflections; for (η^5-C_5H_5)Mo(CO)$_3$Cl, $P2_1/c$, a = 7.9590 (17) Å, b = 10.7180 (28) Å, c = 14.9587 (33) Å, β = 130.968 (15)°, R_F = 2.4% for 1194 reflections; for (η^5-C_5H_5)Mo(CO)$_3$HgCl, $P\bar{4}2_1c$, a = 12.042 (1) Å, c = 15.319 (2) Å, R_F = 4.2% for 1460 reflections. The (η^5-C_5H_5)M(CO)$_3$Cl complexes are isostructural with W–Cl = 2.490 (2) Å and Mo–Cl = 2.498 (1) Å; in contrast to this, the average metal–carbon(ring) distances are W–C = 2.326 Å and Mo–C = 2.304 Å; i.e., the tungsten–ligand distance is less than the molybdenum–ligand distance in the direction of the halide ligand but is greater in the direction of the cyclopentadienyl ligand. In (η^5-C_5H_5)Mo(CO)$_3$HgCl, the average Mo–C(ring) distance is 2.303 Å, with Mo–Hg = 2.683 (1) Å and Mo–Hg–Cl = 160.02 (9)°.

Introduction

While definitive structural studies of [(η^5-C_5H_5)W(CO)$_3$]$_2$ and [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ have been carried out (showing the metal–metal distances W–W = 3.222 (1) Å and Mo–Mo = 3.235 (1) Å)[1] and a large number of structural studies on species containing the [(η^5-C_5H_5)Mo(CO)$_3$] unit have been carried out,[2–12] there have been fewer structural studies of the analogous [(η^5-C_5H_5)W(CO)$_3$]-containing species[13–17] and no comparative studies of simple (η^5-cyclopentadienyl)tricarbonylmetal halides.

---

(1) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(2) (η^5-C_5H_5)Mo(CO)$_3C_2H_5$: Bennett, M. J.; Mason, R. *Proc. Chem. Soc.* **1963**, 273. Bennett, M. J. Ph.D. Thesis, Sheffield University, England, 1965, pp 38–74.

(3) (η^5-C_5H_5)Mo(CO)$_3C_3F_7$: Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213.

(4) [(η^5-C_5H_5)Mo(CO)$_3$][(η^5-C_5H_5)Fe(CO)$_2$]$_2$SnCl: O'Connor, J. E.; Corey, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 3930.

(5) [(η^5-C_5H_5)Mo(CO)$_3$]Mn(CO)$_5$: Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 655.

(6) (η^5-C_5H_5)Mo(CO)$_3CH_2CO_2H$: Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1968**, 1309.

(7) [(η^5-C_5H_5)Mo(CO)$_3$](μ_4-S)[(η^5-C_5H_5)Mo(CO)$_2$][Re(CO)$_3$]$_2$(μ_3-S): Vergamani, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6326.

(8) [(η^5-C_5H_5)Mo(CO)$_3$]$_3$Tl: Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313.

(9) [(η^5-C_5H_5)Mo(CO)$_3$]$_2$Zn and [(η^5-C_5H_5)Mo(CO)$_3$]$_2Zn_2Cl_2(OEt_2)_2$: St. Denis, J.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5427.

(10) [(η^5-C_5H_5)Mo(CO)$_3$]ZnBr(THF)$_2$ and [Bu_4N^+][(η^5-C_5H_5)Mo(CO)$_3^-$]: Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. D. *Inorg. Chem.* **1977**, *16*, 920.

(11) [(η^5-C_5H_5)Mo(CO)$_3$]$_2$Hg: Mickiewicz, M. H.; Raston, C. L.; White, A. H.; Wild, S. B. *Aust. J. Chem.* **1977**, *30*, 1685.

(12) [(η^5-C_5H_5)Mo(CO)$_3$][(η^5-C_5H_5)$_2$Nb]: Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 49.

(13) (η^5-C_5H_5)W(CO)$_3$(σ-C_6H_5): Semion, V. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 1046.

(14) (η^5-C_5H_5)W(CO)$_3$(AuPPh$_3$): Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8.

(15) [(η^5-C_5H_5)W(CO)$_3$]$_3$Ga: Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945.

(16) [(η^5-C_5H_5)W(CO)$_3$]$_2$(AlMe$_2$)$_2$: Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.

(17) (η^5-C_5H_5)W(CO)$_3$(GaMe$_2$): St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1.