Syntheses and X-ray structure determinations of the isomeric pentaphenylethane tricarbonylchromium(0) complexes, 1-tricarbonylchromium(0) phenyl-1,1,2,2-tetraphenylethane and 2-tricarbonylchromium(0) phenyl-1,1,1,2-tetraphenylethane

Bijaya Misra, H.E. Zieger*

The City University of New York, Department of Chemistry, Brooklyn College, Brooklyn, New York 11210 (U.S.A.)

and Jon Bordner*

Crystal and Molecular Structure Laboratory, Pfizer Central Research, Groton, Connecticut 06340 (U.S.A.)

(Received December 16th, 1987)

Abstract

Two chromium tricarbonyl (CTC) coordinated pentaphenylethanes (PPE) have been synthesized via organometallic coupling reactions. X-Ray structure determinations have shown the ethane carbon–carbon bond distances in C(1) and C(2) CTC complexes of PPE to be 1.615 (± 0.007) and 1.620 (± 0.005) Å. Deprotonation of pentaphenylethane with the potassium t-butoxide-n-butyllithium complex gives the pentaphenylethyl carbanion at $-70°C$ in THF as shown by deuteration with CH_3OD to give 2-deuteropentaphenylethane.

Introduction

The coupling reactions of benzylic organolithium carbanions with alkyl- and aryl-substituted alkyl halides have been found to occur with second order kinetics [2a] and predominant inversion of configuration at chiral carbon [2b] except for trityl halide which undergoes electron transfer oxidation to form trityl radicals [3].

During current work on the preparation and reactions of the pentaphenylethyl carbanion [1] we found that some electrophiles caused rupture of the ethane carbon–carbon bond, while others alkylated the aromatic ring rather than react cleanly at the benzylic carbon. D_2O alone gave high yields (87%) of α-deuteropentaphenylethane [4*].

We knew that complexation of one of the aromatic rings on C(2) with a $Cr(CO)_3$ moiety would enhance the acidity of the benzylic hydrogen [5–8] and hoped that it

---

* Reference number with asterisk indicates a note in the list of references.

would stabilize the ethane carbon–carbon bond enough to permit polar reactions at the hindered benzylic carbon without competing electron transfer oxidation [9].

Now we wish to report the syntheses of pentaphenylethane *hapto* C(1) and C(2) tricarbonyl chromium(0) complexes via the coupling reactions of eqs. 1 and 2. In addition, single crystal X-ray structure determinations on benzene solvates of these new compounds permit a comparison of the geometric properties of the new CTC (CTC = $Cr(CO)_3$) complexes with those for uncomplexed pentaphenylethane.

Results

The formation of 2-tricarbonylchromium(0) phenyl-1,1,1,2-tetraphenylethane (**1**) by the reaction of triphenylmethylmagnesium bromide with benzhydryl chloride tricarbonylchromium(0) occurred in 88% yield in a manner analogous to the synthesis of pentaphenylethane [9,10].

$$Ph_3CMgBr \ + \ Ph_2CHCl\text{-}\pi\text{-}Cr(CO)_3 \longrightarrow Ph_3C\text{---}CHPh \qquad (1)$$

(**1**)
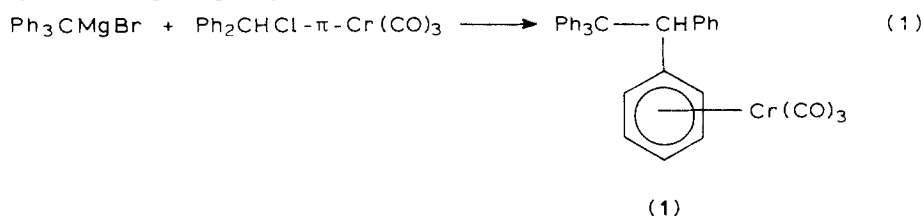
On the other hand, the reaction of the tricarbonylchromium(0) complex of tritylpotassium with Ph_2CHBr to give the isomeric complex, 1-tricarbonylchromium(0) phenyl-1,1,2,2-tetraphenylethane (**2**) in 65.7% yield is a significantly new development among coupling reactions because it shows that the trityl anion chromium(0) complex can displace bromide (but not Cl^-) from the diphenylmethyl

$$Ph_2C:^-K^+ \qquad + \ Ph_2CHBr \longrightarrow Ph_2C\text{---}CHPh_2 \qquad (2)$$

(**2**)
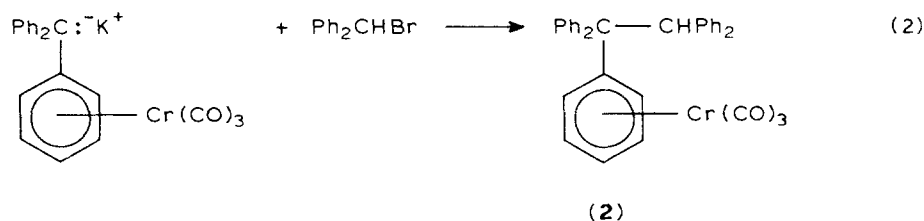
halide system. The carbanion of the CTC complex of triphenylmethane was secured in 85% yield by deprotonation of the hydrocarbon CTC complex with potassium t-butoxide in THF at 25°C.

The structures of **1** and **2** have been confirmed through oxidative removal of the chromium tricarbonyl moiety with ceric ammonium nitrate (CAN) yielding pentaphenylethane, **3** in 78 and 72% yields.

Single crystal X-ray crystallographic analyses of **1** and **2** gave crystal parameters and refinement data shown in Table 1. A comparison of selected bond distance and bond angle data from these analyses with literature data [11] for pentaphenylethane is given in Table 2. The primary difference between pentaphenylethane and complexes **1** and **2** is that the central C(1)–C(2) bond is slightly longer in the chromium tricarbonyl complexes at 1.620 ± 0.005 Å (and 1.615 ± 0.007 Å) than in **3** (1.606 ± 0.003 Å). This difference is all the more remarkable when one considers the near identity of the remaining bond distances and angles of **1** [PPE-π-C_2-Cr(CO)$_3$] shown in the ORTEP diagram of **1** in Fig. 1 and those reported for **3**. Conversely, a comparison of the properties of **2** with **3** shows very good correspondence for bond

Table 1

Single crystal X-ray crystallographic analyses for the isomeric pentaphenylethane-π-Cr(Co)$_3$ complexes

	2	1
A. *Crystal parameters*		
Formula	$C_{35}H_{26}O_3Cr \cdot 1.5C_6H_6$ (663.76)	$C_{35}H_{26}O_3Cr \cdot C_6H_6$ (624.72)
Crystallization medium	benzene/petroleum ether (9/1) at 0 °C	benzene/petroleum ether (1/1) at −17 °C
Crystal size (mm)	$0.20 \times 0.30 \times 0.50$	$0.20 \times 0.22 \times 0.22$
Cell dimensions: a	35.177(5) Å	13.525(3) Å
b	10.663(2) Å	10.678(3) Å
c	18.880(4) Å	22.448(8) Å
α	90.0 °	90.0 °
β	103.71(2) °	92.77(3) °
γ	90.0 °	90.0 °
V	6880(2) Å^3	3238(2) Å^3
Space group	$C2/c$	$P2_1/c$
Molecules/unit cell	8	4
Density calc (g/cm^3)	1.28	1.28
Density obsd (g/cm^3)		1.26
Linear absorption coefficient (cm^{-1})	31.9	31.65
B. *Refinement parameters*		
Number of reflections	5122	3335
N_o, nonzero reflections ($I > 2.0\sigma$)	2929	2785
N_v, no. of variable parameters	404	406
$R\text{-index} = \Sigma\|\|F_o\| - F_c\|\|/\Sigma\|F_o\|$	0.0578	0.053
$GOF = [\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$	1.154	1.41
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.0667	0.0640

Table 2

Bond distances (Å) and bond angles (°) involving the ethane atoms C(1) and C(2) in pentaphenylethane **1** and **2**

| Bond	PPE-π-C(1)-Cr(CO)$_3$	PPE-π-C(2)-Cr(CO)$_3$	PPE [11]
C(1)–C(2)	1.615(7)	1.620(5)	1.606
C(1)–C(9)	1.551(6)	1.533(5)	1.544
C(1)–C(3)	1.545(6)	1.549(5)	1.550
C(1)–C(15)	1.562(7)	1.561(5)	1.563
C(2)–C(21)	1.531(7)	1.535(5)	1.537
C(2)–C(27)	1.528(6)	1.527(5)	1.531
Angle	2	1	PPE
C(2)–C(1)–C(3)	111.2(4)	112.0(3)	114.0
C(2)–C(1)–C(15)	108.4(3)	106.7(3)	107.6
C(2)–C(1)–C(9)	110.5(4)	110.1(3)	109.4
C(3)–C(1)–C(15)	111.0(4)	102.9(3)	102.2
C(3)–C(1)–C(9)	108.7	111.2(3)	110.1
C(9)–C(1)–C(15)	107.0(4)	113.8(3)	113.6
C(1)–C(2)–C(27)	117.5(4)	112.8(3)	113.4
C(1)–C(2)–C(21)	117.9(4)	117.4(3)	118.6
C(21)–C(2)–C(27)	108.6(4)	110.5(3)	109.2
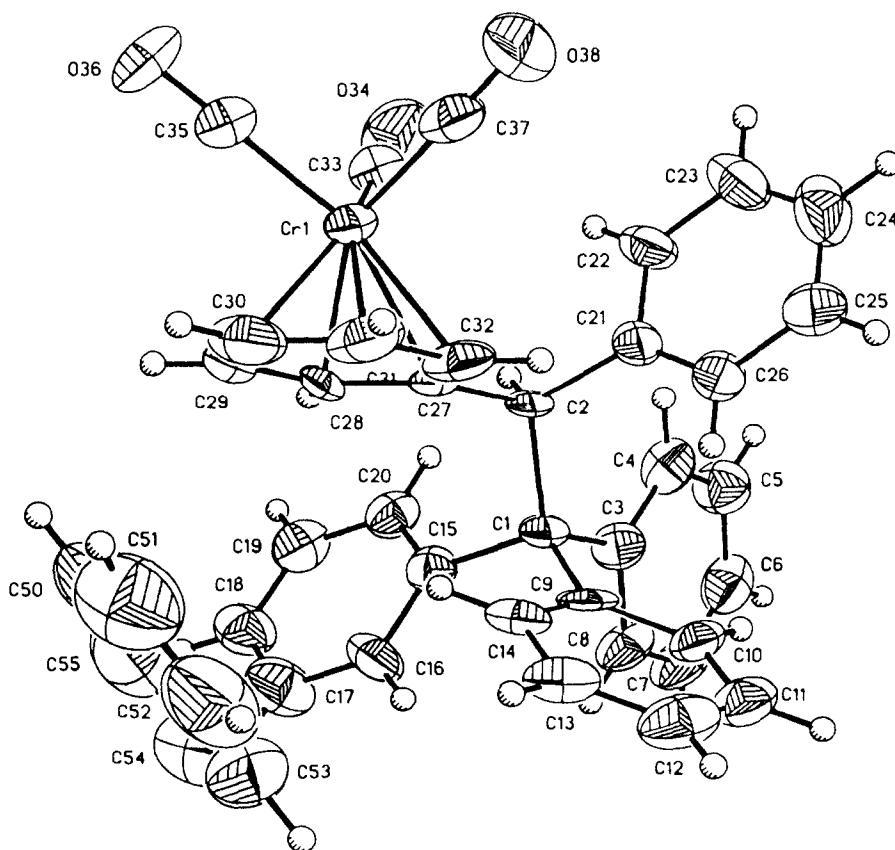
Fig. 1. ORTEP diagram of $1 \cdot C_6 H_6$.

distances and modest changes for the bond angles due primarily to the greater steric congestion caused by introducing the $Cr(CO)_3$ group into the trityl portion of pentaphenylethane.

Figure 2 shows that the $Cr(CO)_3$ grouping in 2 is in the staggered conformation in the sense that the projection of carbon monoxide bonds onto the complexed benzene ring, bisects the ring's carbon–carbon bonds rather than eclipse with the ring carbon atoms. The same staggered conformation is adopted in the solid state by the tricarbonylchromium derivatives of benzene [12,13], hexamethylbenzene [12c,h], phenanthrene, etc., while tricarbonylchromium derivatives of anisole [12d], o-tolui-dine [12e] and methylbenzoate [12d] have eclipsed $Cr(CO)_3$ groups [22].

staggered   syn-eclipsed   anti-eclipsed
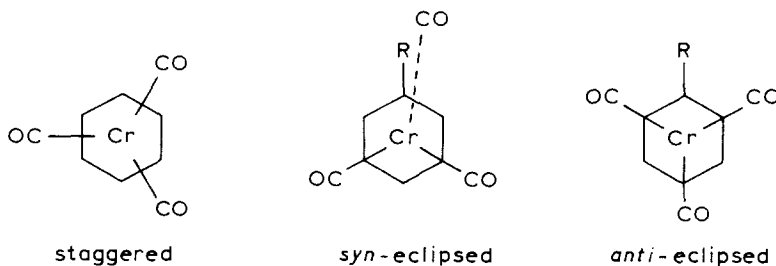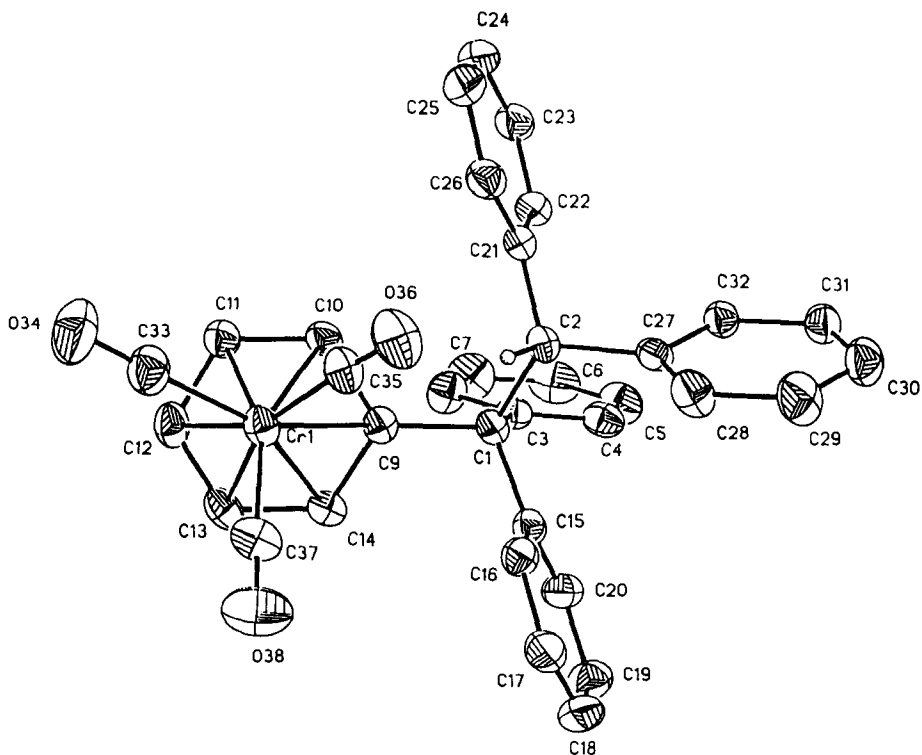
Fig. 2. ORTEP diagram of **2**.

(1)   (2)
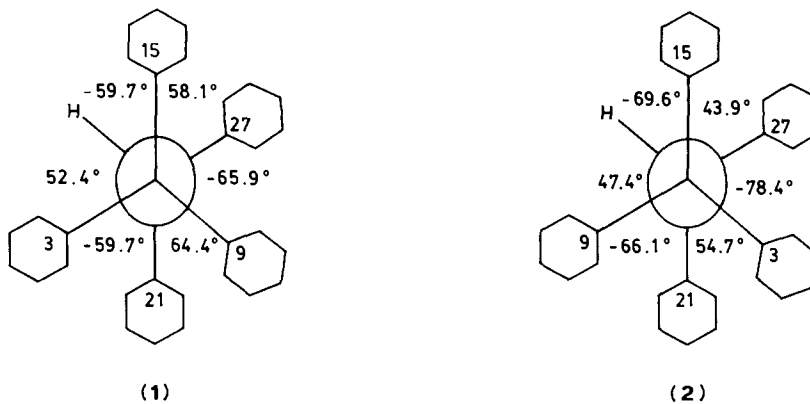
Dihedral angle (°)	Φ_C
C(3) - C(1) - C(2) - H	52.4 (0.3)
H - C(2) - C(1) - C(15)	-59.7 (0.4)
C(15) - C(1) - C(2) - C(27)	58.1 (0.3)
C(27) - C(2) - C(1) - C(9)	-65.9 (0.4)
C(9) - C(1) - C(2) - C(21)	64.4 (0.4)
C(21) - C(2) - C(1) - C(3)	-59.7 (0.4)

Dihedral angle (°)	Φ_C
C(9) - C(1) - C(2) - H	47.4 (0.3)
H - C(2) - C(1) - C(15)	-69.6 (0.3)
C(15) - C(1) - C(2) - C(27)	43.9 (0.5)
C(27) - C(2) - C(1) - C(3)	-78.4 (0.5)
C(3) - C(1) - C(2) - C(21)	54.7 (0.5)
C(21) - C(2) - C(1) - C(9)	-66.1 (0.5)

Fig. 3. Projection of **1** and **2** viewed from C(1) to C(2).

More significant than the preferred conformation in the solid state are the facts that the chromium atom does not bond equally to each carbon atom of the benzene ring and the benzene ring undergoes deformation becoming slightly "bowed" with one bond 4.4 estimated standard deviations (e.s.d.'s) shorter than the 1.40 Å average and the other across the ring 6.1σ longer. In both complexes (1 and 2) the chromium to *ipso* carbon bond is 7–13 e.s.d.'s longer at 2.248 and 2.2727 Å for 1 and 2 than the other five chromium to ring carbon bonds which are reasonably constant at 2.220 Å, respectively.

The dihedral angles, ϕ_C (C(phenyl)–C(1)–C(2)–C(phenyl)) for 1 and 2 are portrayed in Newman projection formulas shown in Fig. 3. In the C(2)-CTC complex, 1, these angles show small deviations ($\pm 6°$) from 60°. However, in complex 2, four of the angles show large deviations from 9.6 to 18.4° similar to the deviations found in pentaphenylethane [11].

NMR spectra

C(2) is a chiral carbon in complex 1. As a result the *ortho* and *meta* carbons of the complexed aromatic ring are magnetically non-equivalent and exhibit six different ^{13}C NMR signals shown in Table 3 (δ 84–112 ppm) Application of the INEPT pulsing sequence [16] provided one-bond and two-bond hydrogen-to-carbon coupling constants. In addition, from the observed multiplicities, chemical shifts for the *ortho, meta* and *para* aromatic ring carbons were assigned. The $^2J(^{13}C_o-H_m)$ 6.6 Hz was observed from the *ortho* carbon to *meta* hydrogen coupling. No coupling (3 bonds) to the benzylic hydrogen was observed. The two-bond coupling in CTC 2

Table 3

^{13}C Chemical shifts (δ (ppm)) and coupling constants (J (Hz)) for Cr(CO)$_3$ complexes 1 and 2

PPE-π-C(2)-CTC (1)		Assignment	PPE-π-C(1)-CTC (2)		PPE (3)
δ	$^1J(^{13}C-H)$		δ	$^1J(^{13}C-H)$	δ (lit. 15)
58.35	127.0	C(2)	59.83	129.5	59.47 (59.9)
63.48	–	C(1)	60.63	–	62.76 (63.1)
86.64	174.7	C_{ortho}-Cr	88.17	175.1	
87.59	174.9	C_{ortho}-Cr			
96.17	170.3	C_{para}-Cr	95.88	172.9	
98.56	176.5	C_{meta}-Cr	98.62	171.1	
100.61	177.0	C_{meta}-Cr			
112.91	–	C_{ipso}-Cr	122.11	–	
126.35		C_{para}	126.28		125.85 (126.0)
127.16		C_{para}	126.93		
127.32		Ph$_3$C-*meta*	127.31		126.94 (127.0)
128.10		Ph$_2$CH-*meta*	127.83		127.37 (127.4)
131.02		Ph$_2$CH-*ortho*	131.46		131.44 [a] (131.9)
(131.41)					
131.57		Ph$_3$C-*ortho*	132.06		131.73 [a] (131.6)
140.06		Ph$_2$CH-*ipso*	142.59		143.09 (143.4)
144.92		trityl-*ipso*	143.07		145.77 (146.0)
232.48		CO	233.08		–

[a] All assignments agree with the lit. values [15] except for the *ortho* carbons which are interchanged.

had the $^2J(^{13}C_o-H_m)$ 7.3 Hz and $^3J(C_o-H_p)$ 0.8 Hz. Assignment of the *ipso* carbon chemical shifts in **3** from their relative intensities was confirmed with the aid of proton coupled spectra which produced the expected multiplets caused by coupling to the *ortho* hydrogens. Coupling of the benzylic hydrogen at C(2) causes the *ipso* carbons at C(2) to appear as a pair of overlapping triplets from which $^2J(^{13}C(2)-H)$ 7.4 Hz can be read from the spectrum.

The ^{13}C NMR spectrum of the pentaphenylethyl, carbanion, **4**, was obtained at $-70°C$. Although changes appeared in the spectrum upon warming to room temperature no signals comparable to those found for authentic Ph_3CLi could be found. Therefore, the decomposition of **4** does not appear to give trityllithium. Work on these anions is in progress and will be reported later.

Discussion

The length of the ethane bond (r_C) in hexaphenylethane (HPE) and its derivatives is a subject of great current interest [17–19]. Calculations show that a value of 1.64 Å is the minimum r_C value to be expected [17d] and hexakis-(3,5-di-t-butylphenyl)ethane is reported to have an ethane bond length of 1.67(3) Å [17a].

The r_C values for the CTC complexes **1** and **2** of PPE at 1.620(5) and 1.615(7) Å are approximately 2.8 and 1.3 e.s.d.'s greater than the literature bond length for **3** [11]. That bonds of this length have enough strength to withstand treatment by oxidizing agents such as I_2/ether or ceric ammonium nitrate is demonstrated by the successful decomplexation of the $Cr(CO)_3$ group to give **3** in good yields.

The presence of the $Cr(CO)_3$ group in **1** permits the abstraction of the benzylic hydrogen with potassium t-butoxide in DMSO. By way of contrast the base needed to deprotonate **3** is $K(O-C[CH_3]_3) + $ n-butyllithium. Deuterolysis with ROD (R = CH_3 or C_2H_5) is effective for both carbanions producing 2-deuteropentaphenylethane. Treatment of the pentaphenylethylcarbanion with numerous electrophiles such as CH_3I, CO_2 and dimethylsulfate has not given pentaphenylethane derivatives to date. Degradation products such as triphenylmethanol and benzophenone have been isolated in one series of runs with copper(I) iodide followed by degassed CH_3I treatment.

Since strenuous efforts were undertaken to exclude dissolved oxygen in the CH_3I and CuI additions to the carbanion solutions, one must conclude that the oxygen atoms gained access to the reaction medium during hydrolysis. The absence of tritylperoxide (or hydroperoxide) suggests H_2O as the source of these oxygen atoms. A possible explanation would involve single electron transfer oxidation of the carbanion to the pentaphenylethyl radical whose instability has been demonstrated by Smith [9].

At the outset of this work we expected the inductive effect of the chromium atom to increase the acidity of the benzylic hydrogen atom. We wondered whether it would also lead to strengthening of the ethane carbon–carbon single bond through reduction of the benzylic character of C(2) caused by re-hybridization from sp^2 to sp^3 of the carbons of the $Cr(CO)_3$ complexed ring. Normally, as the percentage of *s* character in a hybrid orbital decreases, the orbital becomes less like an *s* orbital and the bonding electrons are less tightly held resulting in longer bonds. In our case this would result in longer bonds between the complexed aryl rings and the ethane carbons. No significant lengthening of these aryl ring to ethane carbon bonds was

found. In complex **1** C(2)–C(27) 1.527 Å while the uncomplexed ring had C(2)–C(21) 1.535 Å. For complex **2** the CTC-aryl ring had C(1)–C(9) 1.551 Å and the uncomplexed rings were C(1)–C(15) 1.562, and C(1)–C(3) 1.545 Å. In contrast to this, the ethane carbon–carbon bond is 1.3 to 2.8 e.s.d.'s longer in complexes **1** and **2** than in pentaphenylethane. It remains to be seen whether longer bonds are stronger in these CTC complexes.

Experimental

Melting points were obtained in argon-filled, sealed capillary tubes and are uncorrected. Infrared spectra were run on a Perkin–Elmer Model No. 1320 spectrophotometer. NMR spectra (^{1}H and ^{13}C) were obtained on General Electric QE-300 MHz and Bruker 250 MHz FT NMR spectrometers. Ether, benzene and dioxane were distilled from sodium-benzophenone ketyl before use. Argon (Union Carbide) was purified by passage through BTS catalyst and P_2O_5 drying towers in a Normag® gas purification apparatus.

Triphenylmethyl bromide was prepared from Ph_3COH and acetyl bromide following literature directions [10]. Similarly benzhydryl bromide was obtained from benzhydrol and thionyl bromide (Aldrich Chem. Co.) in 90 % yield. Benzhydryl chloride was obtained in 91% yield from its carbinol with thionyl chloride. Triphenylmethanetricarbonylchromium(0) was obtained in 61% yield by the reaction of triphenylmethane with $Cr(CO)_6$ (Strem Chemicals) in refluxing dioxane for 3 d in an apparatus as described by Strohmeier [14].

Preparation of pentaphenylethyl carbanion and 2-deuteriopentaphenylethane

To a solution of potassium t-butoxide (2.0 g, 20 mmol) and pentaphenylethane (2.05 g, 5 mmol) in THF (75 ml), n-butyllithium (4 ml, 7 mmol) was added dropwise at $-78°$C. An orange-red color formed immediately after addition of the first few drops of n-BuLi. The color deepened to a dark red solution after several minutes. After 2 h of stirring at $-78°$C D_2O or CH_3OD was injected to terminate the reaction. After ether extraction, phase separation and drying, crude pentaphenylethane (2.01 g, 98%) was isolated.

Recrystallization of the crude product from benzene/absolute ethanol (1/3) gave a purified sample of 2-deuterio-pentaphenylethane m.p. 169–172° C (sealed capillary under argon). Integration of the benzylic proton at 5.85 ppm vs. the aromatic multiplet showed the presence of 11 ± 2% of protio pentaphenylethane. That the deuterium atom is located on the benzylic carbon is demonstrated by the ^{13}C NMR spectrum which shows a characteristic 1/1/1 triplet at δ 58.98 ppm whose $^1J(^{13}$C–D) 16.78 Hz.

An IR spectrum in KBr showed a weak C–D stretching band at 2150 cm^{-1} and was otherwise identical with the spectrum for pentaphenylethane.

^{13}C NMR for $C_{32}H_{25}D$: δ 58.98 (t), 62.67, 125.84, 126.93, 127.35, 131.39, 131.69, 143.02, 145.75 in good agreement with the literature [13].

Chemical ionization mass spectroscopy employing NH_3 as a carrier gas showed 10.1% of **3**, 79.7% of 2-deuteriopentaphenylethane and 10.1% of a dideuteriopentaphenylethane.

2-Tricarbonylchromium(0) phenyl-1,1,1,2-tetraphenylethane (1)

Triphenylmethyl bromide (10.029 g, 0.031 mol) in benzene (40 ml) was added to Mg (0.912 g, 0.038 mol) in ether (20 ml) during 10 min. Reaction commenced immediately upon warming and was completed on the steam bath after 2 h. The filtered Grignard reagent was cooled to $10°C$ and was treated with benzhydryl chloride tricarbonylchromium(0), (9.3 g, 0.027 mol) in benzene (30 ml). After stirring at room temperature overnight, the contents of the flask were hydrolyzed with saturated NH_4Cl solution (100 ml). After isolation via ether extraction, drying and solvent removal, the crude residue was recrystallized from benzene/ cyclopentane (1/9) to yield pentaphenylethane-C(2)-tricarbonylchromium(0) (m.p. 178–178.5°C) in 88% yield. The sample was dried in vacuo for 6 h. Anal. Found: C, 76.34, 76.12; H, 5.11, 4.97. $C_{35}H_{26}CrO_3$ calc: C, 76.92; H, 4.76%.

IR (KBr): 1970–1955 and 1905–1860 cm^{-1} (broad CO); ^1H NMR ($CDCl_3$); δ 232.5 (CO), 144.9, 144.1, 131.6, 131.4, 131.0, 128.1, 127.3, 127.2, 126.3, 112.9, 100.6, 98.6, 96.2, 87.6, 86.6, 63.5, 58.4 ppm.

Decomplexation of 1

(a) Iodine method. To a stirred solution of pentaphenylethane-η-C(2)-chromiumtricarbonyl (0.25 g, 0.45 mmol of **1**) in 30 ml of ether at $0°C$, iodine (0.185 g, 0.68 mmol) was added. After stirring for 3 h at $0°C$, washing with 10% $Na_2S_2O_3$ (2×25 ml) and H_2O (2×50 ml), the clear organic layer was separated, dried and evaporated to give 56.9% of pentaphenylethane (0.105 g) whose IR and NMR spectra were indistinguishable from those on an authentic sample. The mixed mp determination was undepressed.

(b) Ceric ammonium nitrate (CAN) method. A 0.5 mmol sample of complex **1** in 10 ml of ether/acetonitrile (1/1) was· stirred with $0.2N$ CAN solution until the yellow solution became nearly colorless. After 0.5 h, hydrolysis and work-up as described under (a) above gave 78% of **3** (0.16 g).

1-Tricarbonylchromium(0) phenyl-1,1,2,2-tetraphenylethane (2)

A solution in THF (20 ml) of the carbanion of the η^6-chromium tricarbonyl complex of triphenylmethane was prepared from 2.05 g (5 mmol) of the complex and potassium t-butoxide (1.7 g, 16 mmol) in 20 min at room temperature. The orange-red carbanion solution was cooled to $0°C$ and 10 ml of a THF solution of diphenylmethyl bromide (2.6 g, 16 mmol) was added during 10 min with a color change to cherry-red. After stirring the reaction mixture overnight at room temperature and hydrolysis with saturated NaCl (200 ml), organic phase was extracted into ether (2×100 ml). The ether solution was dried ($MgSO_4$) and after filtration and solvent removal in vacuo, the dark oily residue was triturated with petroleum ether (3×100 ml) to give an orange-red solid (1.9 g, 65.7%). Recrystallization from benzene/petroleum ether (1/1) gave η^6-C(1)-pentaphenylethanechromium tricarbonyl (**2**) m.p. 182–183°C as a yellow solid.

Anal. Found: C, 76.78; H, 4.76. C, 76.58; H, 4.98. $C_{35}H_{26}CrO_3$ calc: C, 76.92; H, 4.76%.

IR (KBr): 1970–1955, 1965–1860 cm^{-1} (broad, CO); ^1H NMR ($CDCl_3$): δ 7.6–7.0 (m, ArH, 20H), 5.7 (s, benzylic 1H), 5.5–4.5 (m, complexed aromatics, 5H); ^{13}C NMR ($CDCl_3$): δ 233 (CO), 143.1, 142.6, 132.1, 131.5, 127.9, 126.9, 126.3, 122.1, 98.6, 95.9, 88.2, 60.6, 59.8 ppm.

Decomposition of the $Cr(CO)_3$ grouping in **2** with ceric ammonium nitrate gave 72% of pentaphenylethane.

Synthesis of diphenylmethylchloride tricarbonylchromium(0)

Dry HCl was bubbled slowly through a solution of 10.0 g (31 mmol) of benzhydroltricarbonylchromium(0) in anhydrous ether (250 ml) at $-20\,^{\circ}$C for 0.75 h. Excess HCl was chased with dry N_2 gas at $-20\,^{\circ}$C for 1 h. The ether was distilled in vacuo and the residue was recrystallized from petroleum ether benzene (9/1 v/v) to give 9.7 g of benzhydrylchloridetricarbonylchromium(0), 92%, m.p. 76–77$\,^{\circ}$C (dec); lit. 76.5–77.5$\,^{\circ}$C (dec) [20].

IR (KBr), 1980–1945, 1910–1840 (broad CO) cm^{-1}. ^{1}H NMR (CDCl$_3$), 7.35 (m, aromatic 5H), 5.28 (m, 6H); ^{13}C NMR (CDCl$_3$), 232, 138, 129, 128.8, 127.6, 110.4, 93.4, 92.6, 90.8, 90.4, 62.6.

Single crystal X-ray analysis [21]

A representative crystal of **1** was surveyed and a 1-Å data set (maximum sin $\theta/\lambda = 0.5$ was collected on a Nicolet R3m/μ diffractometer. The diffractometer was equipped with a graphite monochromator and copper radiation (λ 1.54178 Å). Atomic scattering factors were taken from the International Tables for X-ray Crystallography [21]. All crystallographic calculations were facilitated by the SHELXTL [23] system. All diffractometer data were collected at room temperature. Pertinent crystal, data collection and refinement parameters are summarized in Table 1.

A trial structure was obtained by direct methods. This trial structure refined routinely. Hydrogen positions were calculated wherever possible. The hydrogen parameters were added to the structure factor calculations but were not refined. The shifts calculated in the final cycle of least-squares refinement were all less than 0.1 of their corresponding standard deviations. The final R-index was 0.053. A final difference Fourier revealed no missing or misplaced electron density.

The single crystal X-ray analysis on 1-tricarbonylchromium(0) phenyl-1,1,2,2-tetraphenylethane (**2**) was run at Columbia University by Dr. Michael Chiang with a Nicolet R3m single crystal X-ray diffractometer. The same SHELXTL software system was used for calculations as in the analysis of **1**.

For compound **2** the data set was collected (sin $\theta/\lambda = 0.544$, $2\theta_{max} = 114\,^{\circ}$) on a Nicolet R3m model diffractometer equipped with a graphite monochromator and employing Cu radiation (λ 1.54178 Å) with a scan speed of 3.91–29.3$\,^{\circ}$/min. The final R-index was 0.0578, $R_w = 0.0667$, with a goodness of fit indicator of 1.154. The ratio of largest shift/esd calculated in the final cycle of least-squares refinement was 0.50.

Supplementary Material Available

Tables of X-ray data on structure determinations of **1** and **2** (15 pages) are available as supplementary material. See NAPS document No. 04567. Order from National Auxiliary Publications Service c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York 10163-3513, Remit in advance $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada add postage of $4.50 for the first 20 pages and $1.00 for each additional 10 pages or $1.50 for microfiche postage.

References and Notes

1 Presented in preliminary form at the 191st National Meeting of the American Chemical Society, paper no. 129, Organic Division, New York City, April 13–18, 1986.

2 H.E. Zieger and D.E. Mathisen, J. Am. Chem. Soc., 101 (1979) 2207; (b) H.E. Zieger, D.A. Bright and H. Haubenstock, J. Org. Chem., 51 (1986) 1180; (c) D.A. Bright, D.E. Mathisen and H.E. Zieger, ibid., 47 (1982) 3521; (d) I. Angres and H.E. Zieger, ibid., 40 (1975) 1457.

3 H.E. Zieger, I. Angres and D. Mathisen, J. Am. Chem. Soc., 98 (1976) 2580; (b) H.E. Zieger, I. Angres and L. Maresca, ibid., 95 (1973) 8201.

4 Integration of aromatic protons at 7.1 ppm vs. the benzylic proton at 5.8 ppm; CMR spectrum (a triplet at 59 ppm) confirms the position of the deuterium at the benzylic carbon.

5 W.R. Trahanovsky and R.J. Card, J. Am. Chem. Soc., 94 (1972) 2897.

6 G. Simonneaux and G. Jaouen, Tetrahedron, 35 (1979) 2249; (b) S. Top, G. Jaouen, B.G. Sayer and M.J. McGlinchey, J. Am. Chem. Soc., 105 (1983) 6426.

7 M.F. Semmelhack, J. Bisha and M. Czarney, J. Am. Chem. Soc., 101 (1979) 769.

8 R.J. Card and W.S. Trahanovsky, J. Org. Chem., 45 (1980) 2555; (b) R.J. Card, W.S. Trahanovsky, J. Org. Chem., 45 (1980) 2560.

9 W.B. Smith and M.C. Harris, J. Org. Chem., 45 (1980) 355; idem, ibid., 48 (1983) 4957.

10 W.E. Bachmann, J. Amer. Chem. Soc., 55 (1933) 3005.

11 R. Destro, T. Pilati and M. Simonetta, ibid., 100 (1978) 6507.

12 (a) P. Corradini and G. Allegra, J. Amer. Chem. Soc., 81 (1959) 2271; (b) M.F. Bailey and L.F. Dahl, Inorg. Chem., 4 (1965) 1314; (c) idem, ibid., 4 (1965) 1298; (d) O.L. Carter, A.T. McPhail and G.A. Sim, J. Chem. Soc. (A), (1967) 228 and 1619; (e) idem, Chem. Commun., (1966) 212; (f) J.C. Boutonnet, F. Rose-Munch, E. Rose, Y. Jeannin and F. Robert, J. Organomet. Chem., 290 (1985) 153; (g) K.R. Stewart, S.G. Levine and A.T. McPhail, ibid., (1984) 45; (h) K. Mislow et al., J. Amer. Chem. Soc., 103 (1981) 6073 and references therein.

13 B. Rees and P. Coppens, Acta Cryst., B 29 (1973) 2515.

14 W. Strohmeier, Chem. Ber., 94 (1961) 2490.

15 T.W. Proulx and W.B. Smith, J. Magn., 23 (1976) 477.

16 G.A. Morris and R. Freeman, J. Amer. Chem. Soc., 101 (1979) 760.

17 B. Kahr, D. Van Engen and K. Mislow, J. Amer. Chem. Soc., 108 (1986) 8305; (b) E. Osawa, Y. Onuki and K. Mislow, ibid., 103 (1981) 7475; (c) D.A. Dougherty and K. Mislow, ibid., 101 (1979) 1402 (d) W.D. Hounshell, D.A. Dougherty, J.P. Hummel and K. Mislow, ibid., 99 (1977) 1916; (e) W.P. Neumann, W. Uzick and A.K. Zarkadis, ibid., 108 (1986) 3762.

18 G. Favini, M. Simonetta and R. Todeschini, ibid., 103 (1981) 3679.

19 M. Stein, W. Winter and A. Rieker, Angew. Chem. Int. Ed. Engl., 17 (1978) 692; (b) W. Winter, T. Butters, A. Ricker and Y. Butsugan, Z. Naturforsch. B, 37 (1982) 955; (c) W. Winter, A. Moosmayer and A. Rieker, ibid., 37 (1982) 1623.

20 J.D. Holms, D.A.K. Jones and R. Pettit, J. Organomet. Chem., 4 (1965) 324.

21 International Tables for X-ray Crystallography; Kynoch: Birmingham, 1962; Vol. 3, pp. 204–214.

22 T.A. Albright, P. Hofmann and R. Hoffmann, J. Amer. Chem. Soc., 99 (1977) 7546.

23 G.M. Sheldrick, in G.M. Sheldrick, C. Krüger and R. Goddard, (Eds.), Crystallographic Computing, 3, Oxford Univ. Press, 1985, p. 175–189 (non vide).