Table XIV. Average Cis C-M-C Bond Angle Data (deg) for the Complexes $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0-4)

complex	CO_{ax}-M-CO_{eq}	CO_{ax}-M-CN	CO_{eq}-M-CO_{eq}	CO_{eq}-M-CN	CN-M-CN
$[Re_2(CO)_{10}]$[a]	93.7 (3)		89.8 (2)		
$[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$	93.3 (8)	92.1 (6)	89.8 (8)	89.9 (7)	
$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$	94.1 (2)	91.1 (2)	90.9 (2)	88.8 (2)	
$[Re_2(CO)_7(CNMe)_3]$[b]	95.7 (7)	93.3 (6)	89.8 (6)	90.1 (6)	86.7 (5)
$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$	94.0 (8)	93.2 (8)	90.2 (8)	88.3 (8)	92.6 (7)

[a] Reference 4. [b] Disordered structure.

Table XV. Average Bond Data (deg) for the M-C-O, M-C-N, and C-N-C Bond Angles of the Complexes $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0-4)

complex	M-C-O_{ax}	M-C-O_{eq}	M-C-N	C-N-C
$[Re_2(CO)_{10}]$[a]	177.5 (7)	178.0 (5)		
$[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$	177.0 (17)	175.9 (17)	175.5 (13)	175.7 (18)
$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$	177.0 (5)	178.3 (5)	177.4 (5)	171.0 (5)
$[Re_2(CO)_7(CNMe)_3]$[b]	173.7 (16)	178.8 (13)	177.9 (13)	176.5 (15)
			174.1 (14)[c]	171.3 (22)[c]
$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$	172.8 (9)	174.9 (20)	176.2 (18)	176.8 (21)

[a] Reference 4. [b] Disordered structure. [c] Average for disordered MeNC ligand.

$(CO)_7(CNMe)_3]$, the conformation adopted in the crystal IIIc (Figures 6 and 8) is probably favored over the other possible conformations IIIa and IIIb (Figure 8) due to packing considerations. In solution all isomers probably coexist.

It has been claimed[37] that packing forces could also be responsible for small deviations in geometry. For example, nonbonded O⋯O interactions could result in M-C-O bonds deviating from linearity by 5-10°.

Acknowledgment. We wish to thank the University and the CSIR for financial support and Mr. J. Albain for collecting the crystallographic data.

Registry No. I, 95463-95-9; II, 95406-94-3; III, 95406-95-4; IV, 95406-96-5.

Supplementary Material Available: Tables of bond lengths, bond angles, and final atomic coordinates for I, isotropic temperature factors for the carbon atoms and anisotropic temperature factors for the non-carbon atoms of I-IV, torsion angles for $[Re_2(CO)_{10-n}(CNR)_n]$, and structure factor amplitudes for I-IV (69 pages). Ordering information is given on any current masthead page.

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Aminobenzenes. 18.[1a] Crystal and Molecular Structures of Novel (Arene)chromium Tricarbonyl Complexes

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Several new (1,3,5-tris(dialkylamino)benzene)chromium tricarbonyl (chromium tricarbonyl = TCC) complexes (2) were prepared and crystal structures for two of them, **2a** ((1,3,5-tripyrrolidinobenzene)TCC) and **2b** ((1,3,5-tripyrrolidino-2-methylbenzene)TCC), were determined to high precision with X-ray data collected from cooled crystals ($T \approx 120$ K). Complex **2a** crystallizes in space group symmetry $P\bar{1}$ with a = 8.7670 (5) Å, b = 10.6023 (8) Å, c = 11.6337 (8) Å, α = 66.724 (6)°, β = 72.560 (6)°, γ = 79.651 (7)°, and Z = 2. For **2b** the space group is $P2_1/c$ with a = 12.323 (1) Å, b = 8.2651 (8) Å, c = 23.902 (2) Å, β = 123.114 (7)°, and Z = 4. The model for **2a** was refined with 13110 contributing reflections to give R_w = 0.053; for **2b** refinement with 9154 reflections gave R_w = 0.058. A crystal structure was also determined for the [(phenyl(trimethylsiloxy)methyl)benzene]TCC complex (**3**) for which the space groups is $P2_1/c$ with a = 6.282 (1) Å, b = 11.319 (4) Å, c = 26.962 (12) Å, β = 93.82 (2)°, and Z = 4 (room temperature). All three complexes display a close approximation to the syn-e conformation for the (arene)TCC moiety. The rotational barriers for compounds **2** could not be established because of their low solubility. The application of conclusions from crystal structures to reaction behavior in solution was proved in the case of the [(phenyl)trimethylsiloxy)methyl)benzene]TCC complex (**3**). The experimental results are in agreement with the reactivity pattern calculated for the crystal structure determined for **3**.

Introduction

The conformation of the chromium tricarbonyl (TCC) group in (arene)TCC complexes has a decisive influence on the reactivity of these compounds; e.g., there is a remarkable regioselectivity in their reactions with electrophiles[2] as well as with nucleophiles.[3] From calculations,

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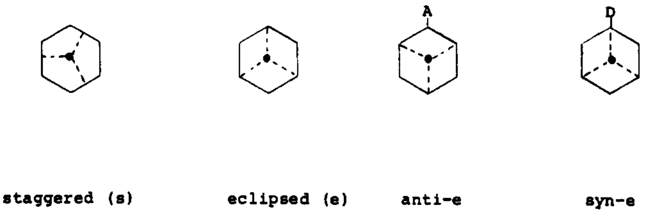
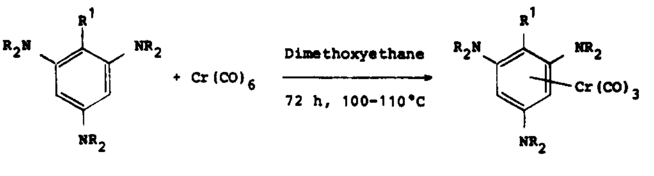
Table I. (1,3,5-Triaminobenzene)TCC Complexes 2 from 1,3,5-Triaminobenzenes 1

benzene	R	R^1	product, (benzene)TCC complex	yield, %
1a, 1,3,5-tripyrrolidino-	$-\mathrm{N}(\mathrm{CH}_2)_4$	H	2a, 1,3,5-tripyrrolidino-	64
1b, 2-methyl-1,3,5-tripyrrolidino-	$-\mathrm{N}(\mathrm{CH}_2)_4$	CH_3	2b, 2-methyl-1,3,5-tripyrrolidino-	53
1c, 2-ethyl-1,3,5-tripyrrolidino-	$-\mathrm{N}(\mathrm{CH}_2)_4$	C_2H_5	2c, 2-ethyl-1,3,5-tripyrrolidino-	52
1d, 1,3,5-tripiperidino-	$-\mathrm{N}(\mathrm{CH}_2)_5$	H	2d, 1,3,5-tripiperidino-	36
1e, 1,3,5-tris(dimethylamino)-	$-N(CH_3)_2$	H	2e, 1,3,5-tris(dimethylamino)-	68

Scheme I



Scheme II



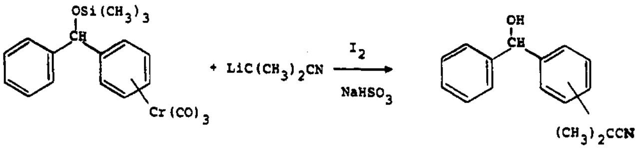
1 2

a correlation between the conformation of the TCC group and the regioselectivity has been deduced.[4] Basic knowledge of the energetic differences of the conformers and the rotational barriers as a function of substituents is most important for the application of TCC complexes in synthesis.

The (benzene)TCC complex exists only in a "staggered" (s) or an "eclipsed" (e) conformation: a crystal structure determination reveals a staggered conformation.[5] In contrast an "anti-eclipsed" (anti-e) and a "syn-eclipsed" (syn-e) conformation also have to be considered for substituted (arene)TCC complexes (Scheme I).[6]

Crystal structure analyses indicate that monosubstituted (arene)TCC complexes with acceptor, A substituents, prefer the anti-e form, while monosubstituted (arene)TCC complexes with donor, D substituents, prefer the syn-e form.[7] Besides electronic factors, steric factors are of great importance in determining the conformation of (arene)-TCC complexes; e.g., for the [1-*tert*-butyl-2,2-(dimethylpropyl)benzene]TCC complex a torsianal angle displaced 44° from the electronically favored syn-e form was found.[7] Because of the low rotational energy barriers in solution, equilibria exist between the possible conformers.[9]

Scheme III



3

4a : meta-
4b : para-

Considerably greater rotational barriers were calculated for the TCC complexes of 1,3,5-triaminobenzenes, 1,3-diazines, and 1,3,5-triazines.[10] In the scope of our research on 1,3,5-triaminobenzenes[11] we have synthesized some (1,3,5-triaminobenzene)TCC complexes 2 (Scheme II) and have determined their crystal structures by single-crystal X-ray diffraction methods.

The low solubility of the complexes 2 did not allow the determination of rotational barriers nor the investigation of structure reactivity relationships. Consequently we have also determined the crystal structure of donor-substituted TCC complex 3[12] and have investigated its reactions in solution (Scheme III). Compound 3 is especially appropriate for testing the suitability of application of conclusions from crystal structures to understanding reaction behavior.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere with degased solvents. IR data were recorded on Perkin-Elmer 221 and 700E spectrometers. ^{1}H NMR spectra were obtained on a Bruker HX 90 spectrometer (trimethylcholorosilane as internal standard). Medium-pressure liquid chromatography: system B. Glatz,[13] silica gel column type B (25 × 2.4 cm) and type C (40 × 4.0 cm) on Lichroprep Merck (0.015–0.025 mm); type B 9400 and type C 7800 theoretical plates; UV detector spectrochrom Gilson. GC–MS spectra: gas chromatograph, Carlo Erba Fractovap 2151AC Special Brechbühler AG, Urdorf; mass spectrometer, Finnigan 4023 with Incos Data System 2300; capillar, 20 m, phase SE-52; reactant gas, CI (methane) and EI (80 eV, source 200 °C). Mass spectra: Varian MAT 711 spectrometer.

(1,3,5-Triaminobenzene)TCC Complexes 2. General Method. The 1,3,5-triaminobenzenes 1 together with chromium carbonyl in dimethoxyethane (DME) or dioxane (destilled from lithium hydride and stored over a molecular sieve (3 Å)) were refluxed under N_2 for 72 h at 100–110 °C. After the solution was cooled, the precipitated crystals were removed by filtration, repeatedly washed with cold ether, and dried under vacuum. In case of 2a and 2b the resulting reaction solutions were concentrated after filtration and purified over silica gel with ethyl acetate/pentane (1/1) as eluent. Complexes 2 were obtained as

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Table II. (1,3,5-Triaminobenzene)TCC Complexes 2 from 1,3,5-Triaminobenzenes 1 and Chromium Carbonyl

			product				anal.				
1, g (mmol)	$Cr(CO)_6$, g (mmol)	solv, (mL)		yield, g[a]	mp, °C	formula		C	H	N	IR ($CHCl_3$) $\nu_{C\equiv O}$, cm^{-1}
1a, 1.78 (6.2)	0.69 (3.1)	DME (40)	**2a**	0.84	300 dec	$C_{21}H_{27}CrN_3O_3$	calcd	59.85	6.46	9.97	1915, 1810
							found	59.65	6.35	10.03	
1b, 0.30 (1.0)	0.20 (0.9)	DME (20)	**2b**	0.209	170 dec	$C_{22}H_{29}CrN_3O_3$	calcd	60.68	6.71	9.65	1920, 1822
							found	60.46	6.63	9.52	
1c, 0.314 (1.0)	0.20	DME (10)	**2c**	0.21	170 dec	$C_{23}H_{31}CrN_3O_3$	calcd	61.46	6.95	9.35	1920, 1825
							found	61.42	7.04	9.16	
1d, 0.328 (1.0)	0.20	DME (10)	**2d**	0.15	300 dec	$C_{24}H_{33}CrN_3O_3$	calcd	62.19	7.18	9.07	1920, 1825
							found	62.23	7.18	8.86	
1e, 0.207 (1.0)	0.20	dioxane (10)	**2e**	0.21	300 dec	$C_{15}H_{21}CrN_3O_3$	calcd	52.47	6.17	12.24	1920, 1830
							found	52.68	6.07	12.33	

[a] Yield (%), see Table I.

Table III. Crystallographic Details for 2a, 2b, and 3

	2a	2b	3
space group	$P\overline{1}$	$P2_1/c$	$P2_1/c$
T, K	~120	~120	297
a, Å	8.7670 (5)	12.323 (1)	6.282 (1)
b, Å	10.6023 (8)	8.2651 (8)	11.319 (4)
c, Å	11.6337 (8)	23.902 (2)	26.962 (12)
α, deg	66.724 (6)	90	90
β, deg	72.560 (6)	123.114 (7)	93.82 (2)
γ, deg	79.651 (7)	90	90
no. of 2θs[a]	60	51	28
angular range,[a] deg	40.02–49.35	34.97–45.78	31.80–57.24
radiatn, Å (graphite monochromator)	0.710 69	0.710 69	1.5418
formula	$C_{21}H_{27}CrN_3O_3$	$C_{22}H_{29}CrN_3O_3$	$C_{19}H_{20}CrO_4Si$
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.479	1.417	1.361
linear abs coeff μ, cm^{-1}	6.61	6.16	58.98
cryst size, mm^3	0.4 × 0.5 × 0.4	0.3 × 0.4 × 0.5	0.1 × 0.2 × 0.4
data collected	$h, \pm k, \pm l$	$h, k, \pm l$	$h, k, \pm l$
no. of unique data	13 630	10 741	3049
no. of observed dat	12 294	7150	2391
2θ "range"	0–85	0–75	0–125
no. of variables refined	362	378	307
no. of contributing reflctns	13 110	9154	2751
$R(F^2)$	0.037	0.045	0.050
$R_w(F^2)$	0.053	0.058	0.064
esd in an observn of unit weight	1.05	1.10	1.23
extinction coeff, × 10^3	2.63		4.10

[a] Number and angular range of the reflections used to refine lattice parameters.

yellow crystalline solids without defined melting points; they are all highly oxidizable compounds.

[(Phenyl(trimethylsiloxy)methyl)benzene]TCC Complex (3). The yellow crystalline solid **3** was prepared by reaction of benzaldehyde with the [(trimethylsilyl)benzene]TCC complex[12,14] and CsF in DMF (see ref 12): ^1H NMR ($CDCl_3$) δ 7.27–7.39 (s, 5 H, Ph), 5.72–5.78 (m, 1 H, Ph), 5.12–5.32 (m, 4 H, Ph), 5.39 (s, CH), 0.07 (s, 9 H, $Si(CH_3)_3$); IR ($CHCl_3$) 1970, 1890 cm^{-1} (C=O), 1250, 880 cm^{-1} $Si(CH_3)_3$); MS (20 eV) *m/e* (relative intensity) 392 (M^+, 29), 308 (M^+, 3 CO, 100). Anal. Calcd: C, 58.15; H, 5.14. Found: C, 58.10; H, 5.10.

2-[(Hydroxyphenylmethyl)phenyl]-2-methylpropionitriles (4a,b). (a) The procedure was analogous to that in ref 3 from **3** (7.85 g, 20.0 mmol), diisopropylamine (2.02 g, 20.2 mmol), 2-methylpropionitrile (1.38 g, 20.0 mmol), 1.43 M *n*-butyllithium/hexane solution (14 mL), and tetrahydrofuran (40 mL). The resulting product (2.18 g, 43%) was identified by GC–MS spectrum as a 9/1 mixture of the two isomers **4a** (meta) and **4b** (para): MS, *m/e* 250 (M – 1), 234 (M – OH), 225 (MH^+ – HCN).

(b) (3-Benzoylphenyl)acetonitrile[15] (5.0 g, 23.0 mmol), methyl iodide (7.7 g, 54.0 mmol), benzyltriethylammonium chloride (0.12 g, 0.05 mmol), and 50% sodium hydroxide solution (60 mL) were vigorously stirred for 3 h at 50 °C, then diluted with water, and extracted with ether. The ether extracts were dried ($CaCl_2$), concentrated, and distilled (bp 208–210 °C (0.7–0.8 mmHg)):[15] yield 3.7 g (66%) of 2-(3-benzoylphenyl)-2-methylpropionitrile; mp 64–70 °C; ^1H NMR ($CDCl_3$) δ 7.4–8.0 (m, 9 H, Ph), 1.8 (s, 6 H, CH_3); IR (KBr) 2400 cm^{-1} (C≡N), 1650 cm^{-1} (C=O). Anal. Calcd: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.87; H, 6.09; N, 5.44.

Sodium borohydride (0.125 g, 3.3 mmol) was added in portions to the stirred solution of 2-(3-benzoylphenyl)-2-methylpropionitrile (0.75 g, 3.0 mmol) in methanol (20 mL); after 30 min water (50 mL) was added, the resulting oily product extracted with ether, and the extract dried ($CaCl_2$) and purified by MPLC with ethyl acetate/ligroin (1/9) as eluent: yield 0.59 g (78%) of oily product. 2-[3-(Hydroxyphenylmethyl)phenyl]-2-methylpropionitrile (**4a**): ^1H NMR ($CDCl_3$) δ 7.1–7.5 (m, 9 H, Ph), 5.7 (d, SCH), 3.6 (d, OH), 1.6 (s, 6 H, CH_3); IR (liquid film) 3460 cm^{-1} (OH), 2230 cm^{-1} (C≡N). Anal. Calcd: C, 81.24; H, 6.82; N, 5.57. Found: C, 18.12; H, 6.79; N, 5.73. The ^1H NMR and IR spectra are in concordance with those of the main product **4a** described in a.

Crystal Structure Determinations. Suitable crystals for **2a** and **2b** were obtained directly from the reaction mixtures; **3** required recrystallization from *n*-hexane. Crystals were sealed in thin-walled glass capillaries; all quantitative X-ray diffraction measurements were made with a Syntex P$\overline{1}$ autodiffractometer equipped with a graphite crystal monochromator. Crystals of **2a** and **2b** were maintained at ca. 120 K with a Syntex LT-1 low-temperature device, that for **3** was maintained at room temperature (24 °C). Crystallographic details for each structure are provided in Table III.

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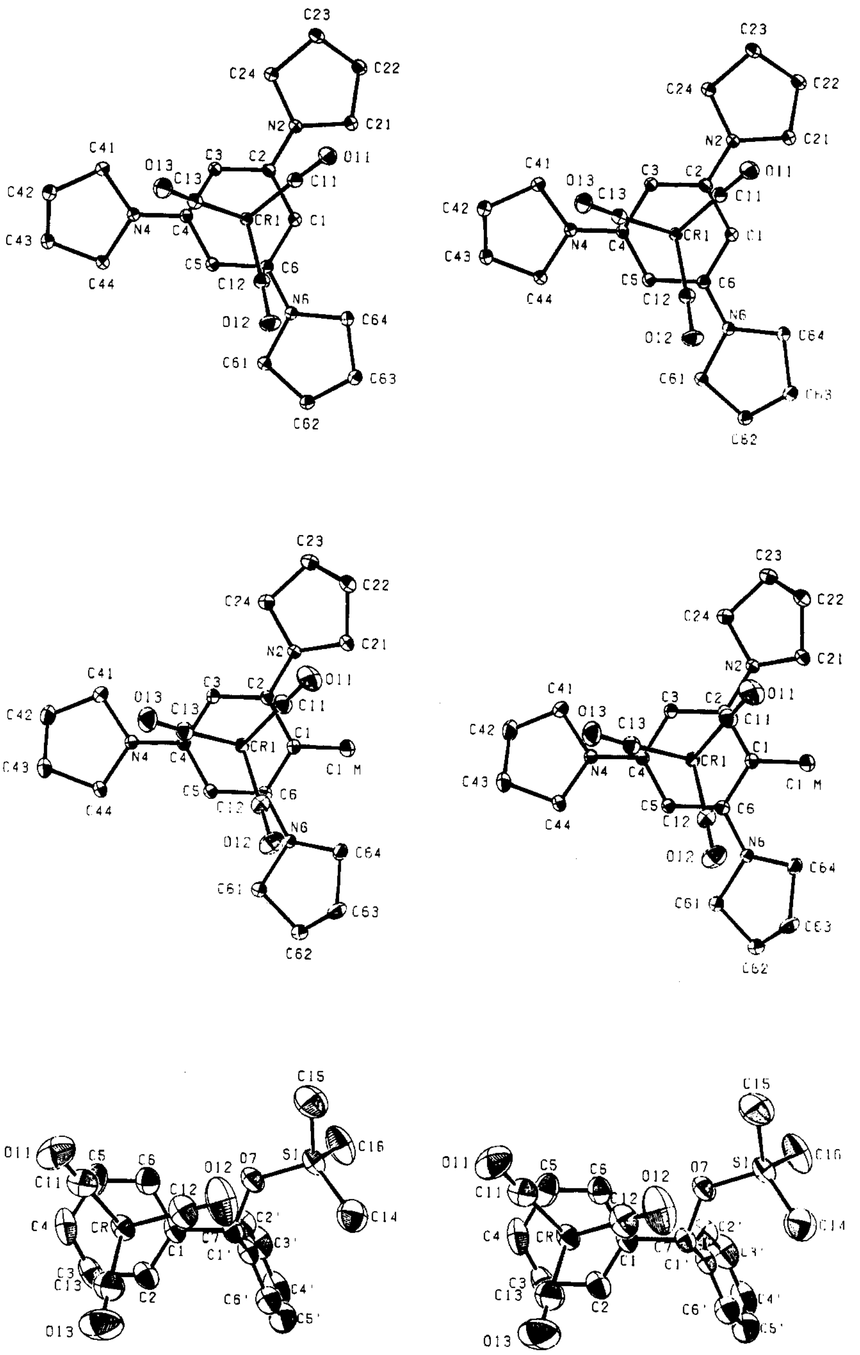

Figure 1. Stereoscopic projections displaying the molecular conformation of **2a**, **2b**, and **3**. Hydrogen atoms have been deleted for clarity. Thermal ellipsoids are presented at the 50% probability level.

Intensities were measured with an ω-scan technique for which the scan range was 0.75°; the scan rate varied from 2.0 to 24.0° min^{-1} (depending on maximum reflection intensity); background radiation was measured on each side of the reflection ($\Delta\omega = 1.0°$) for half the scan time. Three periodically measured reference reflections for each crystal remained constant to within ±5% of their initial values. Data were corrected for Lorentz and polarization effects but not for absorption.

The initial structural models were determined by the heavy-atom method and developed by difference Fourier and least-squares refinement techniques using the XRAY System[16] program library. Neutral atom scattering factors[17,18] were used for all atoms; anomalous dispersion corrections[19] were included for the Cr atoms. Refinement of C, N, O, Cr, and Si atoms was carried out with anisotropic temperature factors; H atoms were refined with isotropic temperature factors. Isotropic extinction corrections were applied to **2a** and **3** but were judged unnecessary on **2b**. The refinement is also characterized in Table III.

Results and Discussion

The refined atomic coordinates from the crystal structure determinations are presented in Table IV; bond distances, bond angles and selected torsion angles are contained in Tables V–VII, respectively. A stereoscopic projection for each molecule is displayed in Figure 1 which also displays the applicable labeling scheme. As is ap-

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Table IV. Atomic Coordinates[a] for 2a, 2b, and 3

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
2a							
Cr1	0.15723 (1)	0.16242 (1)	0.16465 (1)	H1	−0.02976	0.3055	−0.02984
C11	0.11474 (9)	0.32633 (8)	0.18963 (7)	H3	−0.1353	0.01549	0.3342
O11	0.09145 (9)	0.43264 (7)	0.20264 (7)	H5	0.2495	−0.06006	0.05800
C12	0.35800 (9)	0.21031 (8)	0.06572 (7)	H211	−0.3001	0.3817	0.02611
O12	0.48880 (8)	0.23564 (7)	0.00232 (7)	H212	−0.2166	0.4492	0.0967
C13	0.23548 (9)	0.09183 (8)	0.30832 (7)	H221	−0.5355	0.3663	0.1690
O13	0.28381 (9)	0.05309 (8)	0.40099 (7)	H222	−0.4982	0.5125	0.1600
C1	−0.00677 (8)	0.21657 (7)	0.03041 (7)	H231	−0.5654	0.3124	0.3808
C2	−0.11055 (8)	0.16963 (7)	0.15765 (7)	H232	−0.4061	0.3966	0.3416
C3	−0.06719 (8)	0.04311 (7)	0.25038 (7)	H241	−0.2800	0.1842	0.3878
C4	0.05836 (8)	−0.04819 (7)	0.21026 (7)	H242	−0.4059	0.1285	0.3446
C5	0.15844 (8)	−0.00130 (7)	0.08283 (7)	H411	0.02976	−0.1402	0.4632
C6	0.12062 (8)	0.12767 (7)	−0.01047 (6)	H412	−0.08820	−0.2520	0.4655
N2	−0.24607 (8)	0.24566 (6)	0.19144 (6)	H421	0.08906	−0.4028	0.5760
N4	0.08511 (8)	−0.17771 (6)	0.29469 (6)	H422	0.2442	−0.3034	0.4883
N6	0.21016 (8)	0.16705 (6)	−0.13529 (6)	H431	0.1218	−0.4524	0.3820
C21	−0.29311 (9)	0.38226 (7)	0.10614 (7)	H432	0.2931	−0.4542	0.3819
C22	−0.4624 (1)	0.41230 (8)	0.18136 (8)	H441	0.3211	−0.2375	0.2328
C23	−0.4572 (1)	0.33831 (8)	0.32309 (8)	H442	0.2075	−0.2880	0.1821
C24	−0.34611 (9)	0.20875 (7)	0.32438 (7)	H611	0.3293	−0.007360	−0.1639
C41	0.02853 (9)	−0.21781 (8)	0.43601 (7)	H612	0.4364	0.07783	−0.1297
C42	0.1474 (1)	−0.33785 (8)	0.48608 (7)	H621	0.3414	0.1477	−0.3667
C43	0.1997 (1)	−0.40008 (8)	0.38085 (8)	H622	0.5062	0.1515	−0.3609
C44	0.21602 (9)	−0.27220 (7)	0.25722 (7)	H631	0.4497	0.3483	−0.2997
C61	0.35378 (9)	0.08653 (7)	−0.17959 (7)	H632	0.3554	0.3913	−0.4145
C62	0.4051 (1)	0.17065 (8)	−0.32416 (7)	H641	0.1149	0.3299	−0.2659
C63	0.3631 (1)	0.31919 (8)	−0.32910 (8)	H642	0.1924	0.3680	−0.1776
C64	0.20529 (9)	0.31054 (7)	−0.22492 (7)				
2b							
Cr1	0.33232 (2)	−0.01410 (2)	0.08593 (1)	H1M	0.085 (2)	0.300 (3)	0.078 (1)
C11	0.1876 (1)	−0.0596 (2)	0.00477 (7)	H2M	0.194 (2)	0.375 (2)	0.1495 (9)
O11	0.0953 (1)	−0.0984 (2)	−0.04639 (6)	H3M	0.167 (2)	0.450 (2)	0.0804 (8)
C12	0.2805 (1)	−0.1729 (2)	0.11940 (7)	H3	0.458 (1)	0.214 (2)	0.0431 (8)
O12	0.2497 (1)	−0.2765 (1)	0.14110 (6)	H5	0.542 (2)	0.050 (2)	0.2297 (9)
C13	0.4155 (1)	−0.1653 (2)	0.06682 (7)	H211	0.058 (2)	0.409 (2)	−0.0231 (8)
O13	0.4661 (1)	−0.2594 (1)	0.05209 (6)	H212	0.069 (2)	0.225 (2)	−0.0267 (8)
C1M	0.1712 (1)	0.3436 (2)	0.10410 (7)	H221	−0.025 (2)	0.389 (2)	−0.1353 (8)
C1	0.2779 (1)	0.2388 (2)	0.10959 (6)	H222	0.053 (2)	0.249 (2)	−0.1258 (9)
C2	0.3155 (1)	0.2603 (2)	0.06303 (6)	H231	0.150 (2)	0.566 (3)	−0.0888 (9)
C3	0.4364 (1)	0.2001 (2)	0.07807 (6)	H232	0.167 (2)	0.452 (3)	−0.143 (1)
C4	0.5267 (1)	0.1320 (2)	0.14178 (6)	H241	0.305 (1)	0.286 (2)	−0.0558 (8)
C5	0.4841 (1)	0.0970 (2)	0.18479 (6)	H242	0.349 (2)	0.460 (3)	−0.016 (1)
C6	0.3621 (1)	0.1532 (1)	0.16985 (6)	H411	0.689 (2)	0.228 (2)	0.0997 (9)
N2	0.2361 (1)	0.3449 (1)	0.00427 (5)	H412	0.659 (2)	0.044 (2)	0.0811 (9)
C21	0.0930 (1)	0.3291 (2)	−0.03536 (7)	H421	0.884 (2)	0.175 (2)	0.193 (1)
C22	0.0540 (1)	0.3491 (2)	−0.10746 (7)	H422	0.889 (2)	0.046 (3)	0.145 (1)
C23	0.1614 (2)	0.4570 (2)	−0.10031 (8)	H431	0.927 (2)	−0.052 (2)	0.2537 (9)
C24	0.2814 (1)	0.3835 (2)	−0.03964 (7)	H432	0.820 (2)	−0.148 (2)	0.1818 (9)
N4	0.6489 (1)	0.0926 (1)	0.15993 (5)	H441	0.687 (2)	−0.103 (2)	0.2181 (8)
C41	0.6999 (1)	0.1166 (2)	0.11779 (7)	H442	0.765 (2)	0.053 (2)	0.2603 (8)
C42	0.8445 (1)	0.0839 (2)	0.16690 (8)	H611	0.445 (2)	−0.054 (2)	0.2725 (9)
C43	0.8460 (1)	−0.0517 (2)	0.21059 (8)	H612	0.491 (2)	0.122 (2)	0.3086 (9)
C44	0.7341 (1)	−0.0078 (2)	0.21854 (7)	H621	0.327 (2)	0.129 (2)	0.3278 (9)
N6	0.3278 (1)	0.1295 (1)	0.21585 (5)	H622	0.374 (2)	−0.056 (2)	0.3448 (8)
C61	0.4201 (1)	0.0520 (2)	0.28073 (7)	H631	0.223 (2)	−0.135 (3)	0.237 (1)
C62	0.3384 (1)	0.0231 (2)	0.30963 (7)	H632	0.138 (2)	−0.018 (2)	0.252 (1)
C63	0.2105 (2)	−0.0319 (2)	0.24796 (7)	H641	0.148 (2)	0.182 (2)	0.1887 (8)
C64	0.1933 (1)	0.0841 (2)	0.19356 (7)	H642	0.151 (2)	0.038 (2)	0.1493 (8)
3							
Cr	0.4541 (1)	0.02413 (5)	0.18029 (2)	C5′	0.0104 (7)	0.5567 (4)	0.1482 (2)
C11	0.6092 (7)	−0.1115 (3)	0.1740 (1)	C6′	0.0421 (7)	0.4365 (3)	0.1417 (1)
O11	0.7109 (5)	−0.1954 (3)	0.1696 (1)	H2	0.243 (5)	0.226 (3)	0.211 (1)
C12	0.2801 (7)	−0.0198 (4)	0.1255 (2)	H3	0.502 (5)	0.147 (3)	0.275 (1)
O12	0.1735 (6)	−0.0475 (3)	0.0916 (1)	H4	0.793 (6)	0.072 (4)	0.251 (1)
C13	0.2738 (7)	−0.0538 (4)	0.2198 (1)	H5	0.854 (6)	0.089 (3)	0.166 (1)
O13	0.1560 (6)	−0.1023 (3)	0.2442 (1)	H6	0.652 (5)	0.163 (3)	0.109 (1)
C1	0.4156 (6)	0.2109 (3)	0.1545 (1)	H7	0.108 (5)	0.220 (3)	0.1230 (9)
C2	0.3649 (6)	0.2039 (3)	0.2042 (1)	H141	−0.144 (7)	0.164 (4)	0.027 (2)
C3	0.5120 (8)	0.1539 (4)	0.2402 (1)	H142	−0.151 (7)	0.291 (4)	0.041 (1)
C4	0.7065 (8)	0.1121 (4)	0.2275 (2)	H143	−0.162 (6)	0.237 (4)	−0.013 (1)
C5	0.7570 (6)	0.1180 (4)	0.1778 (2)	H151	0.48 (1)	0.163 (7)	−0.020 (2)
C6	0.6164 (6)	0.1675 (3)	0.1418 (1)	H152	0.267 (8)	0.070 (4)	−0.015 (2)
C7	0.2569 (6)	0.2623 (3)	0.1154 (1)	H153	0.247 (8)	0.132 (5)	−0.052 (2)
O7	0.3298 (4)	0.2376 (2)	0.06784 (8)	H161	0.42 (1)	0.421 (6)	−0.025 (2)

Table IV (*Continued*)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Si	0.1959 (2)	0.25095 (9)	0.01319 (3)	H162	0.166 (7)	0.403 (4)	−0.045 (2)
C14	−0.0912 (7)	0.2336 (4)	0.0196 (2)	H163	0.23 (1)	0.441 (6)	0.008 (2)
C15	0.304 (1)	0.1344 (7)	−0.0253 (2)	H2′	0.490 (5)	0.448 (3)	0.099 (1)
C16	0.2518 (8)	0.3969 (4)	−0.0134 (2)	H3′	0.460 (6)	0.640 (4)	0.116 (1)
C1′	0.2291 (6)	0.3947 (3)	0.1237 (1)	H4′	0.131 (7)	0.717 (4)	0.147 (1)
C2′	0.3867 (8)	0.4733 (4)	0.1132 (2)	H5′	−0.120 (6)	0.582 (3)	0.159 (1)
C3′	0.3545 (8)	0.5941 (4)	0.1196 (2)	H6′	−0.067 (6)	0.387 (3)	0.147 (1)
C4′	0.1652 (9)	0.6347 (4)	0.1371 (1)				

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses.

Table V. Bond Distances (A) with Estimated Standard Deviations for 2a, 2b, and 3

bond	**2a**	**2b**	bond	**3**
Cr-C11	1.8290 (9)	1.818 (1)		1.832 (4)
Cr-C12	1.8236 (7)	1.824 (2)		1.847 (4)
Cr-C13	1.8272 (9)	1.826 (2)		1.833 (4)
Cr-C1	2.2752 (9)	2.356 (1)		2.233 (3)
Cr-C2	2.3599 (8)	2.316 (1)		2.218 (4)
Cr-C3	2.2775 (7)	2.253 (1)		2.196 (4)
Cr-C4	2.3457 (8)	2.342 (1)		2.203 (4)
Cr-C5	2.2830 (9)	2.257 (1)		2.184 (4)
Cr-C6	2.3274 (9)	2.295 (1)		2.211 (4)
Cr-O(11)	1.1698 (12)	1.171 (1)		1.155 (5)
C12-O12	1.1740 (9)	1.171 (1)		1.140 (5)
C13-O13	1.1712 (12)	1.167 (2)		1.159 (6)
C1-C2	1.4283 (9)	1.431 (3)		1.402 (5)
C2-C3	1.4236 (9)	1.418 (2)		1.412 (5)
C3-C4	1.4257 (10)	1.422 (2)		1.375 (7)
C4-C5	1.4175 (9)	1.416 (2)		1.398 (6)
C5-C6	1.4275 (8)	1.420 (2)		1.386 (5)
C6-C1	1.4210 (10)	1.421 (2)		1.416 (5)
C1-C1M		1.519 (2)		
C2-N2	1.3573 (9)	1.385 (2)	C1-C7	1.518 (5)
C4-N4	1.3646 (8)	1.360 (2)	C7-O7	1.416 (4)
C6-N6	1.3618 (8)	1.390 (2)	C7-C1	1.528 (5)
N2-C21	1.4653 (9)	1.483 (2)	C1′-C2′	1.374 (6)
N2-C24	1.4650 (9)	1.468 (3)	C1′-C6′	1.383 (5)
N4-C41	1.1711 (10)	1.463 (3)	C2′-C3′	1.395 (6)
N4-C44	1.4639 (10)	1.465 (2)	C3′-C4′	1.387 (7)
N6-C61	1.4671 (9)	1.477 (2)	C4′-C5′	1.361 (7)
N6-C64	1.4674 (8)	1.485 (2)	C5′-C6′	1.388 (6)
C21-C22	1.5301 (11)	1.524 (2)	O7-Si	1.654 (2)
C22-C23	1.5317 (12)	1.526 (3)	Si-C8	1.834 (5)
C23-C24	1.5319 (11)	1.521 (2)	Si-C9	1.836 (7)
C41-C42	1.5321 (11)	1.530 (2)	Si-C10	1.844 (5)
C42-C43	1.5288 (14)	1.525 (3)		
C43-C44	1.5272 (9)	1.535 (3)		
C61-C62	1.5269 (10)	1.519 (3)		
C62-C63	1.5336 (12)	1.525 (2)		
C63-C64	1.5308 (10)	1.534 (2)		

Table VI. Selected Bond Angles (deg) with Estimated Standard Deviations for 2a, 2b, and 3

angle	**2a**	**2b**	angle	**3**
C11CrC12	90.73 (4)	86.83 (7)		88.9 (2)
C11CrC13	87.79 (4)	87.07 (7)		90.2 (4)
C11CrC2	89.96 (3)	92.38 (6)		95.4 (2)
C12CrC13	89.13 (4)	89.77 (8)		89.4 (2)
C12CrC6	86.74 (4)	88.70 (7)		95.1 (2)
C13CrC4	92.04 (3)	87.50 (6)		93.8 (2)
C2CrC6	63.31 (2)	64.37 (5)		66.2 (1)
C2CrC4	63.70 (3)	63.98 (4)		66.6 (1)
C4CrC6	63.87 (2)	64.27 (6)		66.6 (1)
CrC11O11	178.00 (6)	176.0 (1)		178.5 (4)
CrC12O12	177.24 (8)	178.5 (2)		179.6 (4)
CrC13O13	176.55 (8)	177.3 (1)		178.3 (4)
C2C1C6	120.48 (5)	118.9 (1)		118.3 (3)
C1C2C3	118.87 (6)	120.1 (1)		119.9 (4)
C2C3C4	120.15 (6)	120.6 (2)		121.2 (3)
C3C4C5	119.20 (5)	118.3 (1)		118.9 (4)
C4C5C6	120.65 (6)	120.8 (1)		121.0 (4)
C5C6C1	118.93 (6)	120.3 (1)		120.5 (3)
C1C2N2	120.92 (6)	120.1 (1)	C2C1C7	120.4 (3)
C3C2N2	120.19 (6)	119.8 (2)	C6C1C7	121.3 (3)
C3C4N4	120.43 (6)	121.3 (2)	C1C7C1	110.5 (3)
C5C4N4	120.34 (6)	120.3 (1)	C1C7O7	108.4 (3)
C1C6N6	120.74 (5)	120.2 (1)	C1′C7O7	111.9 (2)

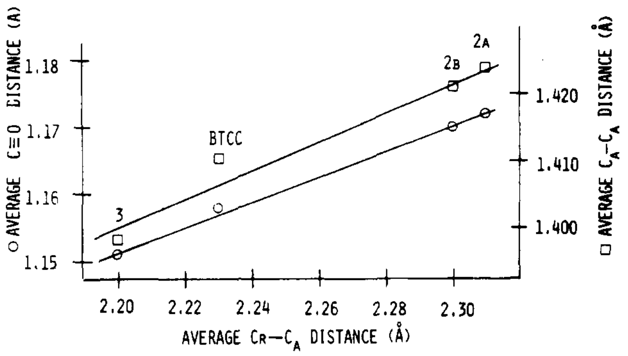

Figure 2. Correlations between the average Cr–C_A bond distances and the average carbonyl C–O bond distances as well as with the average C_A–C_A bond distance. The lines are those defined by the equations in the text.

parent from the figure, the three complexes display close approximations to syn-e conformations. The average C_{CO}–Cr–C_A–N (C_{CO} = carbonyl carbon atom; C_A = arene carbon) torsion angles for **2a** and **2b** are 13.7° and 9.7°, respectively; the C_{CO}–Cr–C_A–C torsion angle is 13.4° for **3**.

The crystal structure determinations for complexes **2a** and **2b** are based on very high-resolution data. Consequently it seems appropriate to compare them with the crystal structure of (benzene)tricarbonylchromium, BTCC, which has also been well determined.[5] Selected, average bond distances are displayed in Table VIII. A graphical presentation of the interrelationship between the average Cr–C_A and the average carbonyl C–O distance is displayed in Figure 2. The data are well described by eq 1 for which r^2 = 0.986.

$$d_{C\equiv O} = 0.733 + 0.190 d_{Cr-C_A} \qquad (1)$$

The clear correlation indicates that the bonding geometry between the Cr atom and the arene ring is determined by electronic rather than steric effects. Taking the Cr–C_A bond distance as indicative of the strength of the metal atom–arene ligand interaction the following trend is apparent: **3** ≥ BTCC ≫ **2b** ≥ **2a**. The average Cr–C_{CO} bond distances are also consistent with this trend in that significantly shorter Cr–C_{CO} bond distances are observed for **2a** and **2b** compared with those for **3** and BTCC. Rees and Coppens[5] point out that there is a dramatic "cis–trans" distinction in the arene C–C bond distances observed for BTCC (C_A–$C_{A(cis)}$ = 1.423 and C_A–$C_{A(trans)}$ = 1.406 Å where cis and trans describe the orientation of the arene bond relative to the Cr–C_{CO} bond). Complexes **2a**, **2b** and **3** also display bonding geometry indicative of such a trend which, though less pronounced, is consistent with the longer bonds

Table VII. Selected Torsion Angles with Estimated Standard Deviations for 2a, 2b, and 3

angle	2a	2b	angle	3
C11CrC2N2	−14.42 (6)	−9.7 (2)	C12CrC1C7	13.4 (3)
C13CrC4N4	−13.10 (7)	−10.7 (1)		
C12CrC6N6	−13.74 (6)	−8.9 (1)		
C6C1C2C3	11.7 (1)	−1.5 (2)		−0.4 (5)
C1C2C3C4	−12.8 (1)	−6.1 (2)		0.4 (6)
C2C3C4C5	11.6 (1)	12.1 (2)		−0.9 (6)
C3C4C5C6	−−9.2 (1)	−10.6 (2)		1.4 (6)
C4C5C6C1	8.1 (1)	3.1 (2)		−1.4 (6)
C5C6C1C2	−9.3 (1)	3.0 (2)		0.5 (5)
C1C2N2C21	−3.5 (1)	−39.6 (2)		
C1C6N6C64	14.0 (1)	2.3 (2)	C6C1C7O7	10.5 (4)
C3C2N2C24	5.0 (1)	−4.9 (2)	C2C1C7C1′	68.3 (4)
C5C6N6C61	−4.0 (1)	0.7 (2)	C1C7C1′C2	72.8 (4)
C3C4N4C41	−20.2 (1)	9.5 (2)	C1C7O7Si	167.2 (2)
C5C4N4C44	−0.3 (1)	42.2 (2)	C6′C1′C2′C3′	−1.5 (5)
N2C21C22C23	31.8 (1)	−28.4 (2)	C1′C2′C3′C4′	0.8 (6)
N2C24C23C22	24.3 (1)	−39.5 (2)	C2′C3′C4′C5′	0.2 (5)
C21C22C23C24	−35.0 (1)	42.1 (2)	C3′C4′C5′C6′	−0.4 (6)
C21N2C24C23	−4.2 (1)	22.5 (2)	C4′C5′C6′C1′	−0.3 (5)
C24N2C21C22	−17.5 (1)	3.8 (2)	C5′C6′C1′C2′	1.4 (5)
N4C41C42C43	−28.7 (8)	36.1 (2)		
N4C44C43C42	−36.1 (1)	24.1 (1)		
C41C42C43C44	40.4 (1)	−37.6 (2)		
C41N4C44C43	19.1 (1)	−1.2 (1)		
C44N4C41C42	6.0 (1)	−22.0 (1)		
N6C61C62C63	35.7 (1)	40.5 (1)		
N6C64C63C62	25.3 (1)	27.6 (2)		
C61C62C63C64	−38.0 (1)	−42.1 (2)		
C61N6C64C63	−2.7 (1)	−2.2 (2)		
C64N6C61C62	−21.0 (1)	−24.1 (1)		

Table VIII. Average Bond Distances for 2a, 2b, BTCC, and 3

bonds	2a	2b	BTCC	3
Cr-C_{arene}	2.3115 (343)[a]	2.303 (39)	2.230 (9)	2.208 (16)
Cr-C_{CO}	1.8266 (22)	1.823 (4)	1.842 (1)	1.837 (7)
C-O_{CO}	1.1717 (17)	1.170 (2)	1.158 (1)	1.151 (8)
C_A-C_A	1.4239 (39)	1.421 (5)	1.414 (9)	1.398 (14)
C_A-$C_{A(cis)}$	1.427 (1)	1.424 (5)	1.420 (1)	1.409 (9)
C_A-$C_{A(trans)}$	1.421 (2)	1.418 (3)	1.406 (1)	1.394 (11)

[a] Numbers in parentheses are standard deviations from the average. They do not reflect the precision in individual values.

being closer to the Cr–C_{CO} bonds. It is also noteworthy that the average C_A–C_A bond length correlates moderately well with the Cr–C_A bond distance. If the fit is made excluding 3 because of apparent thermal motion shortening of the C_A–C_A bond lengths, the eq 2 is obtained for which $r^2 = 0.961$. (see Figure 2).

$$d_{C_A\text{-}C_A} = 0.924 + 0.216 d_{Cr\text{-}C_A} \qquad (2)$$

The ring conformations of **2a** and **2b** are also of interest in that they deviate significantly from planarity (Figure 3). The deviations are clearly toward a chair conformation for **2a** (which does not have the peri interactions between substituents that are present in **2b**); the average absolute value of the endocyclic torsion angles is 10.4°. The atoms "cis" to the Cr–C_{CO} bonds lie very close to the mean plane; the "trans" atoms are displayed toward the Cr atom and the N atoms are on the opposite side of the plane as the Cr atom. For **3** the atoms of the complexed arene are coplanar to within 0.004 Å (σ) and those of the uncomplexed arene to within 0.005 Å.

The reaction of **3** with lithium isobutyronitrile, under analogous conditions to those reported by Semmelhack et al.,[3c] affords a 9/1 mixture (overall yield 43%) of the benzhydrols **4a** and **4b**, with the meta isomer as the main product. This result is in agreement with extended Hückel molecular orbital calculations of Albright et al.[4] for the site of nucleophilic attack on (arene)TCC complexes, according to which regioselective attack on the arene should be controlled by the conformation of the $Cr(CO)_3$ unit.

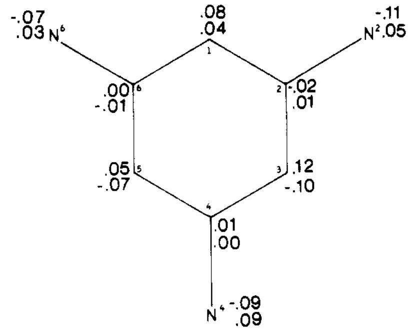

Figure 3. Deviations from the least-squares mean plane fit to the nine atom fragments indicated. The upper values are for **2a** (σ = 0.08 Å) and the lower ones for **2b** (σ = 0.06 Å).

Preferential attack by nucleophiles in charge-controlled as well as in overlap-controlled reactions[4] should occur on arene carbons which eclipse chromium–carbonyl bonds,[4] that means in the case of the reaction of **3** at the meta position to the alkyl substituent. The alkyl substituent in **3** is expected to be only of minor influence on the orientation of nucleophilic addition.

This result also allows the conclusion that the reaction behavior of complex **3** in solution corresponds with the behavior expected from the crystal structure determined.

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Registry No. **1a**, 16857-93-5; **1b**, 20758-47-8; **1c**, 20758-48-9; **1d**, 16857-95-7; **1e**, 16857-99-1; **2a**, 95421-47-9; **2b**, 95464-51-0; **2c**, 95421-48-0; **2d**, 95421-49-1; **2e**, 95421-50-4; **3**, 76862-03-8; **4a**, 95421-51-5; **4b**, 95421-52-6; $Cr(CO)_6$, 13007-92-6; $LiC(CH_3)_2CN$, 50654-53-0; [(trimethylsilyl)benzene]TCC, 33248-13-4; benzaldehyde, 100-52-7; 2-methylpropionitrile, 78-82-0; (3-benzoylphenyl)acetonitrile, 21288-34-6; 2-(3-benzoylphenyl)-2-methylpropionitrile, 60566-76-9.

Supplementary Material Available: Listings of structure factor amplitudes, hydrogen atom parameters, anisotropic temperature factors, and equations for least squares planes (183 pages). Ordering information is given on any current masthead page.

Control of Slippage and Conformation in Indenyl Complexes

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A systematic approach and rationalization of the departure of cyclopentadienyl groups from the classical symmetrical η^5-arrangement is presented. Slippage of the metal from the center to one side of the five-membered ring is shown to be a common occurrence. Furthermore, the direction of the slippage and the conformation of the indenyl ring relative to the other substituents on the metal can be predicted by using simple trans effect arguments. The effects of slippage and conformation on NMR parameters are illustrated. The structures of two complexes were determined by X-ray crystallographic analysis. Crystal data for $(\eta^5\text{-}C_9H_7)Mo(CO)_2(\eta^2\text{-}1\text{-}CH_3C_3H_4)$: space group $P2_1/n$; $a = 11.978$ (3) Å, $b = 7.992$ (1) Å, $c = 14.109$ (4) Å; $\beta = 91.85$ (3)°; $V = 1350.1$ (9) Å^3; $M_r = 322.22$; $Z = 4$; $\rho_{calcd} = 1.59$ g cm^{-3}. For 1364 reflections with $F^2 \geq 3\sigma(F^2)$, $R_1 = 0.033$ and $R_2 = 0.034$. Crystal data for $[(\eta^5\text{-}C_9H_7)IrH\{P(C_6H_5)_3\}_2]BF_4\cdot CH_2Cl_2$: space group $P2_1/n$; $a = 12.895$ (2) Å, $b = 12.285$ (3) Å, $c = 26.566$ (6) Å; $\beta = 94.08$ (2)°; $V = 4198$ (3) Å^3; $M_r = 1004.69$; $Z = 4$; $\rho_{calcd} = 1.59$ g cm^{-3}. For 3717 reflections with $F^2 \geq 3\sigma(F^2)$, $R_1 = 0.046$ and $R_2 = 0.054$.

In this paper we attempt to systematize and rationalize the departure of cyclopentadienyl groups from the classical symmetrical η^5-arrangement. Such departures are important because they represent a way of producing coordinative unsaturation and thus enhancing the reactivity of η^5-cyclopentadienyl complexes. For example, the rates of substitution reactions of some coordinatively saturated η^5-indenyl complexes are rapid compared with their η^5-cyclopentadienyl analogues.[1-4] This has been attributed to the ease of slippage of the metal from the center of the ring to one side and the formation of a more reactive η^3-indenyl intermediate. The sideways displacement of the metal is presumably facilitated in the indenyl complex by the recovery of some of the resonance energy in the benzene ring.

As early as 1966, the second-order component of the rate expressions for carbonyl substitution by phosphine in η^5-CpRh(CO)$_2$ was attributed to formation of a η^4-Cp intermediate.[3] Renewed interest in slippage from η^5-Cp to η^3-Cp and eventually conversion to the η^1-Cp complex has arisen owing to recent observations that treatment of η^5-CpMo(CO)$_2$(NO), η^5-CpW(CO)$_2$(NO), η^5-CpRe(CO)$_3$, and η^5-CpRe(CO)(NO)(CH$_3$) gave η^1-Cp products rather than carbonyl substitution upon treatment with Me$_3$P.[5-10]

Although the existence of the η^3-Cp group had previously been suggested to be mythical[11] or to not correspond to a plausible molecular state,[12] the X-ray structure of (η^5-Cp)W(CO)$_2$(η^3-Cp) showed conclusively that an unambiguously η^3-Cp structure could exist as an isolable species.[13] A key feature in the (η^5-Cp)W(CO)$_2$(η^3-Cp) structure is the folding of the uncomplexed C═C fragment out of the plane of the the allyl fragment to produce an *envelope angle* of $\Omega = 20°$. It is this folding of the C$_5$ ring that provides one approach to assigning η^3-character to a system. As the five-membered ring flattens, the unequivocal distinction between an η^5- and an η^3-Cp fades[11,12] and delineation as one of these extremes becomes unwarranted. Nevertheless, small distortions from five-fold symmetry occur in η^5-Cp complexes which can be rationalized by electronic effects arising from the other ligands on the metal.[14]

The resonance energy gained in the distortion to a allyl–ene type five-membered ring in indenyl complexes has a profound effect on their chemistry and the stability of various conformations of the ring relative to the other ligands on the metal. The question of conformational

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