In memory of T. A. Stephenson

Dinitrogen Complexes derived from Tricarbonyl(η^6-hexaethylbenzene)-chromium(0): Crystal and Molecular Structure of μ-Dinitrogen-bis[dicarbonyl(η^6-hexaethylbenzene)chromium(0)]–Toluene (1/1)†

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Photolysis under nitrogen of toluene solutions of mixtures of tricarbonyl(η^6-hexaethylbenzene)-chromium(0), (**1**), and diphenylacetylene gave dicarbonyl(dinitrogen)(η^6-hexaethylbenzene)-chromium(0), (**2**), and μ-dinitrogen-bis[dicarbonyl(η^6-hexaethylbenzene)chromium(0)], (**3**), as the only identifiable organometallic products. A decoalescence phenomenon observed in the 90.56-MHz ^{13}C-{^{1}H} solution n.m.r. spectrum of (**3**) is attributed to slowed ethyl group rotation and a barrier ($\Delta G^{\ddagger}_{300}$) of 46.0 ± 3.0 kJ mol^{-1} for this process has been determined from lineshape fitting studies. The crystal and molecular structure of (**3**) has been determined and the molecule shown to be a dinitrogen-bridged dinuclear chromium complex with C_{2h} molecular symmetry. The co-ordinated hexaethylbenzene has been found to adopt a 1,3,5-distal-2,4,6-proximal methyl conformation.

Usually one carbonyl group of a tricarbonyl(η^6-arene)chromium(0) molecule can be readily exchanged to give [Cr(η^6-arene)(CO)$_2$L] (L = substituted phosphine or alkene) by photolysis under nitrogen of a solution of the organometallic species and stoicheiometric amounts of the replacement ligand L. Although there is the possibility that alkynes may polymerise under these conditions, in general they react in an analogous manner to alkenes. Therefore as part of our ongoing studies of the stereochemical and stereodynamical properties of η^6-hexaalkylbenzene complexes[1] we attempted the replacement, under standard conditions, of one carbonyl of tricarbonyl(η^6-hexaethylbenzene)chromium(0), (1), with diphenylacetylene. In this case, however, the only isolable organometallic species did *not* contain co-ordinated diphenylacetylene or any of its derivatives but rather were the dinitrogen complexes, dicarbonyl(dinitrogen)(η^6-hexaethylbenzene)chromium(0), (2), and μ-dinitrogen-bis[dicarbonyl(η^6-hexaethylbenzene)chromium(0)], (3). The synthesis of analogous dinitrogen complexes has previously been achieved by the photolysis of tricarbonyl(η^6-mesitylene)chromium(0) or tricarbonyl(η^6-hexamethylbenzene)chromium(0) in tetrahydrofuran (thf) solution under nitrogen,[2] but neither the structures of these complexes nor the activation of a replaceable carbonyl group by diphenylacetylene have been reported previously.

Results and Discussion

As indicated by Karsch,[3] almost all transition metals are known to form complexes with molecular nitrogen, but notably for chromium the examples are relatively few. Moreover, with the exception of *trans*-[1,2-bis(dimethylphosphino)ethane]bis(dinitrogen)chromium(0), (4),[4] all reported chromium dinitrogen complexes are rather labile and decompose more or less rapidly in solution at room temperature. We were therefore surprised to isolate from the photolysis of toluene solutions of (1) and diphenylacetylene, dark red crystals of (3), obtained when the photolysis was performed under a static blanket of nitrogen, and orange crystals of (2), obtained when nitrogen was bubbled through the solution during the period of the photolysis. Photolysis of (1) with no diphenylacetylene present caused the toluene solution to turn orange but removal of the solvent gave only yellow-green crystals of the unchanged initial complex. Likewise, unchanged starting materials were obtained from photolysis with only trace amounts of diphenylacetylene present. Approximately 1:1 mole ratios of (1) and diphenylacetylene were required to obtain reasonable yields of the dinitrogen complexes. As to the fate of the diphenylacetylene, neither organometallic species involving the co-ordinated alkyne nor polymeric materials, in particular tetraphenylcyclopentadienone, originating from this molecule could be identified. Only unchanged diphenylacetylene was isolated from the reaction mixture. We therefore consider that the role of diphenylacetylene in these photolyses is similar to that previously reported for thf:[2] equations (1)—(3).

$$\underset{(1)}{[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_3]} + \mathrm{PhC{\equiv}CPh} \xrightarrow{h\nu} [\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_2(\mathrm{PhC{\equiv}CPh})] + \mathrm{CO} \quad (1)$$

$$[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_2(\mathrm{PhC{\equiv}CPh})] + \mathrm{N_2} \longrightarrow \underset{(2)}{[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_2(\mathrm{N_2})]} + \mathrm{PhC{\equiv}CPh} \quad (2)$$

$$2[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_2(\mathrm{PhC{\equiv}CPh})] + \mathrm{N_2} \longrightarrow \underset{(3)}{[\{\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6Et_6})(\mathrm{CO})_2\}_2(\mathrm{N_2})]} + 2\mathrm{PhC{\equiv}CPh} \quad (3)$$

The complex [Cr(η^6-C$_6$Me$_6$)(CO)$_2$(PhC≡CPh)] is isolable but rather unstable.[5] It seems plausible that our inability to isolate [Cr(η^6-C$_6$Et$_6$)(CO)$_2$(PhC≡CPh)] results from additional instability caused by the steric effect of the ethyl groups.[1]

Although the orange crystals of (2) were apparently of reasonable quality, disorder in the crystal precluded the determination of the crystal and molecular structure of this compound. Attempts at recrystallisation caused decomposition of the sample.

No band attributable to nitrogen–nitrogen stretching was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Bond distances (Å) and angles (°) for complex **(3)**

N(1)–Cr	1.917(9)	C(5)–Cr	2.245(12)	C(4)–C(3)	1.416(12)	C(7)–C(6)	1.478(22)
C(1)–Cr	1.820(10)	C(1)–O(1)	1.146(11)	C(8)–C(3)	1.524(13)	C(9)–C(8)	1.524(14)
C(2)–Cr	2.214(13)	N(1)–N(1)	1.110(18)	C(5)–C(4)	1.409(10)	C(11)–C(10)	1.522(14)
C(3)–Cr	2.192(8)	C(3)–C(2)	1.400(11)	C(10)–C(4)	1.552(13)	C(13)–C(12)	1.524(20)
C(4)–Cr	2.229(8)	C(6)–C(2)	1.540(20)	C(12)–C(5)	1.492(19)		

C(1)–Cr–N(1)	91.4(4)	C(5)–Cr–C(1)	137.1(3)	C(4)–C(3)–C(2)	118.3(9)	C(10)–C(4)–C(5)	120.6(8)
C(2)–Cr–N(1)	161.3(4)	C(5)–Cr–C(2)	77.4(5)	C(8)–C(3)–Cr	129.9(6)	C(4)–Cr–C(4)	66.5(5)
C(2)–Cr–C(1)	102.2(4)	C(5)–Cr–C(3)	67.0(3)	C(8)–C(3)–C(2)	121.4(8)	C(4)–C(5)–C(4)	120.3(13)
C(3)–Cr–N(1)	133.2(3)	C(5)–Cr–C(4)	36.7(3)	C(8)–C(3)–C(4)	120.2(9)	C(4)–C(5)–Cr	71.0(6)
C(3)–Cr–C(1)	86.8(4)	O(1)–C(1)–Cr	176.2(9)	C(3)–Cr–C(3)	68.1(5)	C(12)–C(5)–Cr	130.8(9)
C(3)–Cr–C(2)	37.1(3)	C(1)–Cr–C(1)	85.6(6)	C(3)–C(2)–C(3)	122.5(14)	C(12)–C(5)–C(4)	119.9(6)
C(4)–Cr–N(1)	98.7(4)	C(3)–C(2)–Cr	70.6(6)	C(3)–C(4)–Cr	69.9(5)	C(7)–C(6)–C(2)	119.0(13)
C(4)–Cr–C(1)	103.1(4)	C(6)–C(2)–Cr	131.9(9)	C(5)–C(4)–Cr	72.3(6)	C(9)–C(8)–C(3)	113.3(9)
C(4)–Cr–C(2)	65.9(3)	C(6)–C(2)–C(3)	118.7(6)	C(5)–C(4)–C(3)	120.1(9)	C(11)–C(10)–C(4)	115.8(8)
C(4)–Cr–C(3)	37.4(3)	C(2)–C(3)–Cr	72.3(6)	C(10)–C(4)–Cr	132.2(6)	C(13)–C(12)–C(5)	113.0(12)
C(5)–Cr–N(1)	83.9(5)	C(4)–C(3)–Cr	72.7(5)	C(10)–C(4)–C(3)	119.2(9)	Cr–N(1)–N(1)	180.0(10)

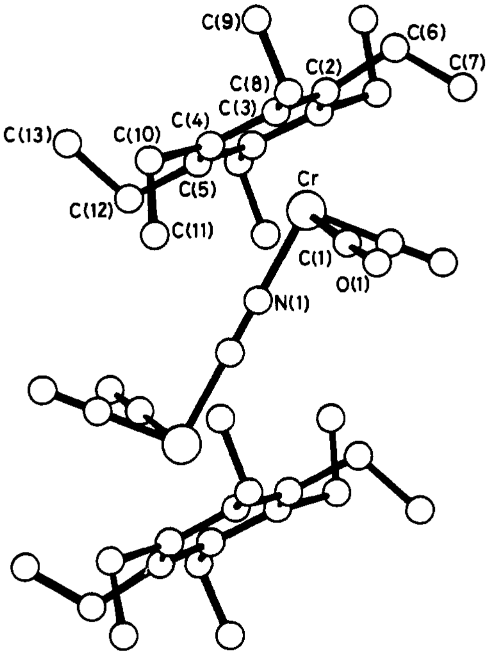

Figure. The molecular structure of complex **(3)**

observed in the i.r. spectrum of **(3)**, consistent with a centrosymmetrical molecular structure for this and the analogous mesitylene and hexamethylbenzene dinitrogen-bridged complexes.[2] Dark red, air-stable crystals of **(3)**, suitable for *X*-ray analysis were obtained from toluene solution at 0 °C. As far as we are aware there has been no previous structural determination of a dinitrogen-bridged dinuclear chromium complex and **(4)** is the only other stable chromium(0) dinitrogen complex to have been fully structurally characterised.[4]

The Figure shows the C_{2h} molecular symmetry of **(3)**. Both **(4)** and **(3)** have crystallographically-imposed symmetry; crystals of **(4)** are triclinic, space group $P\bar{1}$, with one molecule per unit cell; those of **(3)** are monoclinic, space group $C2/m$, with two molecules per unit cell and with the σ_h plane of one molecule coincident with a crystallographic mirror plane. Crystallographically imposed symmetry does not require the Cr–N–N units of either **(3)** or **(4)** to be linear and the structures of the two molecules enable valid and precise comparisons to be made of the N–N bond distances and Cr–N–N angles in terminal-dinitrogen and bridging-dinitrogen chromium(0) complexes. In **(4)** the N–N bond distance is only 0.985(4) Å,[4] significantly shorter than those of either **(3)** [1.110(18) Å, Table 1] or of N_2 itself (1.0987 Å).[6] The Cr–N–N moiety of **(4)** is only approximately linear with an angle of 177.3(2)° and it may be that this slight bending is the result of steric interactions with the atoms of the 1,2-bis(dimethylphosphino)ethane (dmpe) ligands. The corresponding moiety for **(3)** is more closely linear, with a Cr–N–N angle of 180.0(10)°. One further small difference is a slightly longer chromium–nitrogen bond distance in **(4)** [1.957(4) Å][4] than in **(3)** [1.917(9) Å].

Each of the hexaethylbenzene moieties of **(3)** adopts the same stereoisomer, (*a*),* as do **(1)** and free hexaethylbenzene with the methyl groups projecting alternately above and below the benzene ring plane.[7] The C_{arene}–CH_2–CH_3 planes are likewise essentially perpendicular to the ring plane. The chromium tripodal ligands efficiently eclipse the benzene ring carbons bearing the alkyl groups distal to the metal atom. The C_{arene}–CH_2–CH_3 bond angles of the eclipsed and non-eclipsed ethyl groups differ appreciably: those of the eclipsed (distal) groups are very similar to each other and average 113.2°, those of the non-eclipsed (proximal) groups are significantly larger and vary from 115.8(8) [C(4)–C(10)–C(11)] to 119.0(13)° [C(2)–C(6)–C(7)], suggestive of steric strain imposed by the $Cr(CO)_2N_2R$ moiety.

Both **(2)** and **(3)** decompose rapidly in CD_2Cl_2 solution. Fortunately, **(3)** is sufficiently stable in [$^2H_8$]toluene solution to observe the low-temperature 90.56-MHz ^{13}C-{^1H} sub-spectra of its arene and carbonyl carbons, but not those of the alkyl carbons which were obscured by the solvent CD_3 resonance. The carbonyl carbon resonance at δ 234.1 remained a singlet down to the lowest temperature observed. In contrast, the singlet arene carbon resonance at δ 109.0 observed at ambient temperature decoalesced so that at temperatures below 218 K two sharp signals of equal intensity at δ 106.5 and 115.5 were observed. No further decoalescence of these signals was observed down to 173 K, below which temperature the solution froze. The observed spectrum is consistent with the retention in solution of the C_6Et_6 stereoisomer of the crystal, the coalescence phenomenon reflecting a topomerisation of the molecule in which the non-eclipsed and eclipsed ethyl groups undergo site exchange. Rates of exchange were obtained by lineshape analysis using the DNMR3 program,[8] and a least-squares fit of the rate data to the Eyring equation yielded a value of $\Delta G^{\ddagger}_{300}$ =

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* We retain the previously described[7] conformational descriptors (*a*)—(*h*) for the eight possible C_6Et_6 stereoisomers.

Table 2. Atomic co-ordinates for the non-hydrogen atoms of (**3**)

Atom	*x*	*y*	*z*
Cr	0.141 0(2)	0.0000	0.399 1(2)
O(1)	0.250 5(7)	0.132 4(6)	0.575 1(7)
N(1)	0.032 1(8)	0.0000	0.478 1(9)
C(1)	0.205 9(8)	0.083 5(7)	0.505 4(8)
C(2)	0.227 1(10)	0.0000	0.255 1(11)
C(3)	0.178 6(7)	0.083 0(6)	0.254 4(7)
C(4)	0.074 7(6)	0.082 6(6)	0.236 5(7)
C(5)	0.023 2(9)	0.0000	0.227 9(10)
C(6)	0.338 6(12)	0.0000	0.261 1(16)
C(7)	0.407 1(13)	0.0000	0.381 3(17)
C(8)	0.234 3(8)	0.172 1(7)	0.262 4(9)
C(9)	0.242 6(9)	0.209 3(9)	0.138 8(11)
C(10)	0.018 4(8)	0.173 8(7)	0.222 4(9)
C(11)	0.003 2(9)	0.216 7(8)	0.339 8(10)
C(12)	−0.086 2(11)	0.0000	0.209 5(12)
C(13)	−0.138 3(13)	0.0000	0.075 8(14)
C(14)	0.518 5(25)	0.081 2(18)	0.030 0(27)
C(15)	0.552 1(24)	0.042 5(20)	0.086 4(30)
C(16)	0.593 2(28)	0.053 6(26)	0.159 8(35)

46.0 ± 3.0 kJ mol^{-1}. This value is similar to those obtained for ethyl group rotation in other metal complexes of hexaethylbenzene.[1]

Although accidental isochrony cannot, of course, be discounted as its cause, the observed lack of a further decoalescence in the arene carbon signals of (**3**) would seem to preclude the possibility of hindered rotation about the chromium–arene bond as has been proposed for dicarbonyl(η^6-hexaethylbenzene)(thiocarbonyl)chromium(0);[9] however, this has been questioned.[1]

Experimental

Variable-temperature N.M.R. Measurements.—The variable-temperature ^{13}C-{^{1}H} n.m.r. spectrum of (**3**) was recorded at 90.56 MHz on a Bruker WH360 spectrometer operating in the Fourier-transform mode. The concentration of the sample in [$^2H_8$]toluene solution was 45 mmol dm^{-3} and this was filtered under N_2 through a grade 3 glass sinter, freeze-thaw degassed, and sealed in a 10-mm (outside diameter) tube. The temperature of the probe was measured by a thermocouple inserted in an n.m.r. tube filled with toluene to the same depth as the solution in the sample tube. Temperatures were considered accurate to ±2 °C.

Synthesis.—*Tricarbonyl*(η^6-*hexaethylbenzene*)*chromium*(0), (**1**). This was prepared as described previously.[7]

Dicarbonyl(*dinitrogen*)(η^6-*hexaethylbenzene*)*chromium*(0), (**2**). This complex was prepared by u.v. irradiation (1 h) of a toluene solution of (**1**) (0.44 g, 1.15 mmol) and diphenylacetylene (0.18 g, 1.00 mmol). Dissolved oxygen was removed prior to the photolysis by bubbling nitrogen through the solution for 30 min and the flow of gas was continued during the subsequent u.v. irradiation. The orange solution was filtered under N_2, concentrated to about half its original volume, and left at 0 °C overnight. Orange crystals were deposited and filtered off under N_2. Attempts at recrystallisation caused decomposition of the sample (Found: C, 63.1; H, 7.8; N, 7.5. Calc. for $C_{20}H_{30}CrN_2O_2$: C, 62.8; H, 7.9; N, 7.3%).

μ-*Dinitrogen-bis*[*dicarbonyl*(η^6-*hexaethylbenzene*)*chromium*(0)], (**3**). This complex was prepared by the same procedure as that for (**2**) except that N_2 was not bubbled through the solution during the period of the photolysis. The dark red solution was filtered under N_2, concentrated to about half its original volume, and left at 0 °C overnight. Dark red crystals were deposited and filtered off under N_2 (Found: C, 67.2; H, 7.8; N, 3.6. Calc. for $C_{40}H_{60}Cr_2N_2O_4{\cdot}C_7H_8$: C, 68.1; H, 8.3; N, 3.4%).

Crystallography.—Crystals of (**3**), $C_{40}H_{60}Cr_2N_2O_4{\cdot}C_7H_8$, $M = 829.2$, obtained from toluene solution at 0 °C as air-stable, red-brown tablets with prominent {001} faces, are monoclinic, space group $C2/m$, $a = 13.923(10)$, $b = 14.800(12)$, $c = 11.265(9)$ Å, $\beta = 102.48(5)°$, $U = 2\,266$ Å^3, $Z = 2$, $D_c = 1.09$ g cm^{-3}, $F(000) = 888$, Cu radiation ($\lambda = 1.5418$ Å), $\mu = 43.0$ cm^{-1}.

Data were collected photographically from three crystals, all measuring *ca.* 0.4 × 0.4 × 0.2 mm, mounted on the *b*, *c*, and *ab* axes (layers 0—3, 0—2, 0—5, respectively). Equi-inclination multi-film Weissenberg exposures were scanned by the S.E.R.C. Microdensitometer Service, Daresbury Laboratory. The merging *R* value was 0.066 before absorption correction, 0.062 after, for 909 unique data. A Patterson synthesis indicated that the space group was either $C2/m$, with the Cr atom on a mirror plane, or $C2$. The analysis was initiated in $C2$, and completed in $C2/m$ after the mirror symmetry had become apparent. No PhC≡CPh moieties could be detected; instead, Cr atoms related by an inversion centre were found to be linked by a linear Cr–X–X–Cr bridge, the X_2 unit refining satisfactorily as N_2. In addition, three peaks could be refined with site occupation factor 0.5 as C atoms of a toluene molecule which was disordered about the inversion centre at 0.5,0,0 with two mirror-related orientations for its ring plane. The ethyl H atoms were included at calculated positions in the last cycles of full-matrix least-squares refinement, which converged at $R = 0.068$, $R'\{= [\Sigma w(\Delta F)^2/\Sigma wF^2]^{\frac{1}{2}}\} = 0.085$ (toluene C atoms isotropic, other non-H atoms anisotropic, 909 data, 133 parameters, $w = 1$). The maximum and minimum departures from planarity in the final difference map were +0.49 and −0.57 e Å^{-3}. The SHELX 76 program[10] system was used in all calculations.

Bond lengths and angles are given in Table 1, final atomic co-ordinates are in Table 2.

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