W_3(O-*i*-Pr)$_9$(Cl)$_2$(μ_3-CMe). An Unexpected Mode of μ_3-Ethylidyne Bonding and Dynamic Solution Behavior

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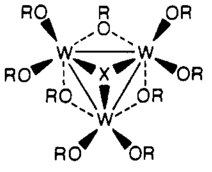
From the reaction between $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9$ and either $(PhCN)_2PdCl_2$ or C_2Cl_6 (1 equiv) in hydrocarbon solutions at room temperature, the compound $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9(Cl)_2$ (1) has been obtained. In the solid state, compound 1 has a molecular structure involving a triangle of metal atoms with two W–W bonding distances, 2.553 (2) and 2.707 (2) Å, and one long, 3.41 (1) Å, nonbonding distance. An unexpected structural feature of 1 is that the alkylidyne ligand bridges the two non M–M bonded W atoms in a nearly symmetrical manner, utilizing C_{sp^2} hybrids, but is relatively weakly bonded, using mostly carbon p orbital character, to the third (hinge) tungsten atom. Compound 1 shows temperature-dependent NMR spectra (^1H and ^{13}C) with low-temperature-limiting spectra consistent with the solid-state structure. However, the variable-temperature spectra require a site exchange between two of the tungsten atoms. Crystal data for 1 at −137 °C: $a = 20.833$ (9) Å, $b = 20.368$ (11) Å, $c = 9.702$ (3) Å, $Z = 4$, $d_{calcd} = 1.91$ g cm^{-3}, and space group $P2_12_12_1$.

Introduction

We have now shown that an extensive organometallic chemistry can be supported by alkoxide clusters of Mo and W[1] and are currently interested in using these clusters as "ligands" to mononuclear complexes of the late transition metals, M′. We envisage three types of initial interaction: (i) weak alkoxide bridge formation to M′, (ii) metal–metal bond formation between the Mo/W cluster and M′, and (iii) metal–carbon, M′–C, and metal–metal bond formation, M′ to Mo/W, between the Mo/W alkoxide cluster and M′. In each case the subsequent reactivity of the heterometallic cluster should be of interest.

The trinuclear $W_3(\mu_3\text{-CMe})(\mu_2\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$ cluster[2] provides a suitable starting point for this type of investigation. Its molecular structure is depicted by A.



A, X = CMe

Note there are (i) three μ-O-*i*-Pr ligands that could act as tripodal ligands, (ii) three pairs of terminal RO ligands that could act as chelating ligands involving either 4- or 5-membered rings, (iii) six electrons involved in W–W bonding, and (iv) six electrons involved in binding the capping alkylidyne to the W_3 center.

Results and Discussion

Synthesis of $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9(Cl)_2$. The reaction between $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9$ and the substitutionally labile[3] $(PhCN)_2PdCl_2$ failed to yield an isolable adduct of any of the aforementioned types. Instead, the reaction proceeds according to the stoichiometry shown in eq 1.

$$W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9 + (PhCN)_2PdCl_2 \xrightarrow[C_6D_6]{25\ ^\circ C} \underset{1}{W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9(Cl)_2} + Pd(m) + 2PhCN \quad (1)$$

Although no intermediates were observed, a W_3Pd adduct of one of the types mentioned above or a complex with W–Cl–Pd bridges are both plausible intermediates in the formation of 1.

The formation of 1 in eq 1 indicated that $PdCl_2$ was merely involved in a redox reaction wherein two clorine atoms were transferred to the W_3 cluster, and thus a more direct route to 1 should be available. Indeed the reaction between $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9$ and C_2Cl_6 in hexane proceeds to give 1 in a 45% yield. Reactions of $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9$ with $(PhCN)_2PtCl_2$ and $HgCl_2$ also provide 1.

Solid-State and Molecular Structure of $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9(Cl)_2$. The molecular structure of 1 found in the solid-state is shown in Figure 1. This view, looking nearly perpendicular to the plane of the three W atoms, emphasizes the opening up of the triangle, W(1)–W(2)–W(3) = 81°, and the retention of the μ_3-CMe ligand. Fractional coordinates are given in Table I, and selected bond distances and angles are listed in Table II. The local geometry about W(1) is pseudo-trigonal-bipyramidal while both W(2) and W(3) are in pseudooctahedral environments and share a common face formed by two alkoxide ligands and the ethylidyne ligand. The W–W distances, W(1)–W(2) = 2.71 Å and W(2)–W(3) = 2.55 Å, are understandable in terms of the availability of four electrons to form two metal–metal single bonds. The W(1)-to-W(3) distance is 3.41 (1) Å, clearly indicative of a non M–M bonding distance.[4]

There are several unusual and noteworthy features associated with the structure of 1. In particular, it seems surprising that the μ_3-ethylidyne ligand should have been retained and that the shorter W–C distances, W(1)–C(42) = 1.98 (2) Å and W(3)–C(42) = 2.09 (2) Å, involve the non M–M bonded tungsten atoms. Furthermore, the methyl carbon of the ethylidyne ligand lies only 0.24 Å out of the plane formed by W(1), C(42), and W(3). This implies that the μ_3-alkylidyne carbon atom is principally sp^2-hybridized and that the W(2)–C(42) bond utilizes a high degree of carbon p character (W(2)–C(42) = 2.20 (2) Å).

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(1) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Smith, C. A. *Organometallics* 1987, *6*, 1280 and references therein.

(2) (a) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Huffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* 1985, *107*, 1234. (b) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. *Organometallics* 1986, *5*, 2384.

(3) Kharasch, M. S.; Seyler, R. C., Mayo, F. R. *J. Am. Chem. Soc.* 1938, *60*, 882.

(4) This is typical of a $M_2(\mu\text{-OR})_2$ non M–M bonded distance, see: Chisholm, M. H. *Polyhedron* 1983, *2*, 681.

(5) I.e., in preference to μ_2-CMe and μ_3-O-*i*-Pr or an alternate more open structure involving only μ_2-CMe and μ_2-O-*i*-Pr ligands. There are, however, several examples of compounds with grossly asymmetric μ_2- or μ_3-alkylidyne ligands. For example, $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$: Os–C(alkylidyne) = 2.035 (8), 2.035 (8), and 2.586 (10) Å. Yeh, W.-Y.; Shapley, J. R.; Li, Y.; Churchill, M. R. *Organometallics* 1985, *4*, 767.

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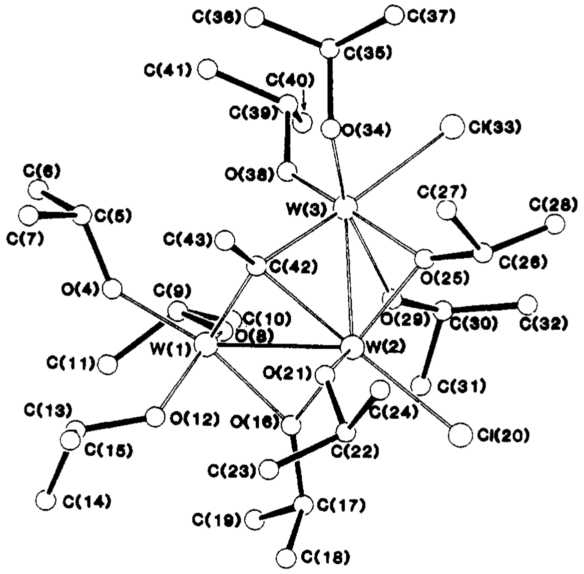


Figure 1. Ball-and-stick drawing of the $W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}CMe)(Cl)_2$ molecule. Pertinent bond distances (Å) and angles (deg), averaged where appropriate: W(1)–W(2) = 2.7074 (18); W(2)–W(3) = 2.5530 (17); W(1)–C(42) = 1.983 (23); W(2)–C(42) = 2.199 (24); W(3)–C(42) = 2.092 (22); W–O(terminal) = 1.89 (4); W–O(bridging) = 2.05 (5); W–Cl = 2.46 (3); W(1)–W(2)–W(3) = 80.75 (6); W(1)–C(42)–W(2) = 80.5 (9); W(2)–C(42)–W(3) = 73.0 (7); W(1)–C(42)–W(3) = 113.6 (12).

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9(Cl)_2$

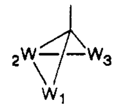
atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å
W(1)	-6838.9 (5)	-4013 (1)	-3557 (1)	12
W(2)	-7577.0 (5)	-2920 (1)	-3478 (1)	12
W(3)	-8430.5 (5)	-3777 (1)	-2906 (1)	12
O(4)	-6639 (8)	-4827 (8)	-2710 (18)	17 (3)
C(5)	-6876 (14)	-5267 (14)	-1699 (31)	26 (6)
C(6)	-6884 (13)	-5942 (14)	-2332 (29)	23 (5)
C(7)	-6467 (14)	-5269 (14)	-407 (30)	22 (6)
O(8)	-7174 (8)	-4434 (8)	-5095 (18)	15 (3)
C(9)	-7135 (12)	-5074 (12)	-5714 (27)	13 (5)
C(10)	-7494 (14)	-5037 (15)	-7130 (33)	29 (6)
C(11)	-6422 (14)	-5265 (14)	-5916 (31)	22 (6)
O(12)	-6024 (8)	-3710 (9)	-3008 (19)	22 (4)
C(13)	-5457 (15)	-4013 (16)	-2419 (33)	32 (7)
C(14)	-4951 (15)	-4099 (15)	-3659 (33)	31 (6)
C(15)	-5239 (16)	-3629 (18)	-1202 (38)	43 (8)
O(16)	-6844 (8)	-3160 (8)	-4675 (18)	16 (3)
C(17)	-6475 (14)	-2815 (14)	-5714 (32)	27 (6)
C(18)	-5956 (15)	-2389 (15)	-5102 (34)	27 (6)
C(19)	-6213 (15)	-3335 (15)	-6650 (36)	33 (7)
Cl(20)	-7662 (3)	-1865 (3)	-4642 (8)	23
O(21)	-7098 (7)	-2504 (8)	-2046 (18)	12 (3)
C(22)	-6799 (13)	-1893 (13)	-1841 (28)	24 (6)
C(23)	-6094 (16)	-2051 (17)	-1377 (39)	41 (7)
C(24)	-7140 (16)	-1581 (16)	-601 (37)	38 (7)
O(25)	-8464 (8)	-2761 (8)	-2596 (17)	14 (3)
C(26)	-8744 (12)	-2195 (12)	-1947 (26)	14 (5)
C(27)	-8688 (14),	-2297 (15)	-375 (32)	26 (6)
C(28)	-9375 (13)	-2048 (15)	-2530 (30)	26(6)
O(29)	-8243 (8)	-3344 (8)	-4765 (17)	12 (3)
C(30)	-8564 (13)	-3290 (13)	-6111 (27)	18 (5)
C(31)	-8052 (13)	-3249 (13)	-7223 (31)	20 (5)
C(32)	-9042 (13)	-2712 (13)	-6062 (27)	19 (5)
Cl(33)	-9598 (3)	-3739 (3)	-3480 (8)	21
O(34)	-8702 (8)	-3888 (8)	-1044 (17)	17 (4)
C(35)	-9175 (13)	-4276 (13)	-416 (28)	19 (5)
C(36)	-8888 (16)	-4730 (17)	627 (38)	39 (8)
C(37)	-9681 (15)	-3862 (17)	212 (35)	35 (7)
O(38)	-8435 (8)	-4641 (8)	-3561 (21)	20 (3)
C(39)	-8909 (14)	-5141 (15)	-3712 (34)	28 (6)
C(40)	-8654 (15)	-5745 (15)	-2948 (36)	32 (7)
C(41)	-9007 (18)	-5328 (17)	-5139 (40)	44 (8)
C(42)	-7491 (10)	-3788 (12)	-2145 (26)	10 (4)
C(43)	-7346 (14)	-3754 (15)	-635 (29)	24 (6)

Table II. Bond Distances (Å) and Angles (deg) for $W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9(Cl)_2$

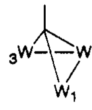
A	B	dist
W(1)	W(2)	2.7074 (18)
W(1)	O(4)	1.896 (16)
W(1)	O(8)	1.857 (17)
W(1)	O(12)	1.883 (17)
W(1)	O(16)	2.047 (17)
W(1)	C(42)	1.983 (23)
W(2)	W(3)	2.5530 (17)
W(2)	Cl(20)	2.432 (7)
W(2)	O(16)	1.979 (17)
W(2)	O(21)	1.909 (17)
W(2)	O(25)	2.062 (17)
W(2)	O(29)	2.057 (16)
W(2)	C(42)	2.199 (24)
W(3)	Cl(33)	2.496 (6)
W(3)	O(25)	2.093 (16)
W(3)	O(29)	2.045 (16)
W(3)	O(34)	1.907 (17)
W(3)	O(38)	1.872 (17)
W(3)	C(42)	2.092 (22)

A	B	C	angle
W(2)	W(1)	C(42)	53.2 (7)
W(1)	W(2)	W(3)	80.75 (6)
W(1)	W(2)	Cl(20)	138.97 (18)
W(1)	W(2)	C(42)	46.3 (6)
W(3)	W(2)	Cl(20)	130.82 (18)
W(3)	W(2)	C(42)	51.6 (6)
W(2)	W(3)	Cl(33)	127.50 (18)
W(2)	W(3)	C(42)	55.4 (7)
W(1)	C(42)	W(2)	80.5 (9)
W(1)	C(42)	W(3)	113.6 (12)
W(1)	C(42)	C(43)	123.2 (18)
W(2)	C(42)	W(3)	73.0 (7)
W(2)	C(42)	C(43)	123.6 (20)
W(3)	C(42)	C(43)	122.3 (18)

NMR Studies. The low-temperature-limiting NMR spectra are consistent with the observed solid-state structure. At −20 °C the ^1H NMR spectrum has nine distinct septets for the methine protons of the O-*i*-Pr ligands. The ^{13}C NMR of the labeled compound $W_3(\mu\text{-}{}^*CMe)(O\text{-}i\text{-}Pr)_9(Cl)_2$ ($^*C$ = 99 mol % ^{13}C) at −20 °C shows three distinct coupling constants to ^{183}W ($I = {}^1/_2$, 14.5% natural abundance): $^1J_{^{183}W-^{13}C}$ = 117.5, 98.8, and 47.7 Hz. On the basis of bond distances and considerations of hybridization, these coupling constants may reasonably be assigned to W(1), W(3), and W(2), respectively. When the temperature is raised, two of the satellites, due to coupling to ^{183}W, broaden and then merge. See Figure 2. The large one bond coupling of 117.5 Hz[6] is not involved in this exchange. It thus appears that the two tungsten atoms with chloride ligands (W(2) and W(3)) are undergoing site exchange while the third is not involved. The most viable mechanism to account for this behavior involves the interconversion of structures B and C, diagramatically depicted below. The motion requires the migration of M–M bonds from W(1)–W(2) to W(1)–W(3) with concomitant motion of the μ_3-alkylidyne ligand and alkoxide ligands. This process is an enantiomerization, and no W–C bonds are broken, but rather while the short W(1)–C(42) bond is maintained, the W(2) to C(42) and W(3) to C(42) bonds



B



C

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[6] This may be compared with $^1J_{^{183}W-^{13}C}$ = 126 Hz in $W_3(\mu_3\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$.

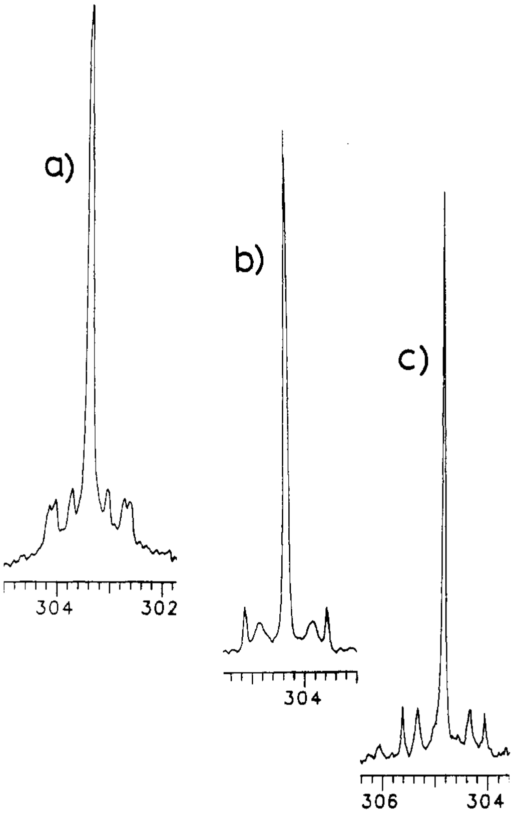

Figure 2. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of the alkylidyne region of $W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}^{13}CMe)(Cl)_2$: (a) −20 °C; (b) 22 °C; (c) 37 °C. At higher temperatures decomposition occurs at a significant rate.

are exchanged. There is evidently extensive alkoxide scrambling during this process, though a high-temperature-limiting ^1H NMR spectrum is not attained at 37 °C in toluene-d_8. Above this temperature decomposition becomes rapid.

From the above it is evident that the fluxional process, though not uniquely defined, must involve migration of a M–M bond. As noted sometime ago by Muetterties[7] this is not a commonly encountered mechanism in cluster carbonyl chemistry, though there are well-documented examples. For example, Shapley et al.[8] noted such a process for the molecule $CpWOs_3(CO)_{10}(\mu_3\text{-}CAr)_2(\mu\text{-}H)$, where Ar = tolyl.

While we have not lost sight of our initial goal, the present study serves to illustrate that the choice of metal–ligand bonds for the late transition metal, M′, may greatly influence or dominate the course of reaction with Mo/W alkoxide clusters.

Experimental Section

Reagents and General Techniques. Dry, oxygen-free solvents and atmospheres (N_2) were used for all manipulations. Reactions were run and samples handled by using standard Schlenck and drybox techniques. The compounds $W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9$[2] and $(PhCN)_2PdCl_2$[3] were prepared as reported earlier.

^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (^1H, 300 MHz; ^{13}C 75.4 MHz) in dry, oxygen-free benzene-d_6 or toluene-d_8. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 283 spectrometer.

Table III. Summary of Crystal Data

empirical formula	$C_{29}H_{66}Cl_2O_9W_3$
color of cryst	black
cryst dimen (mm)	0.08 × 0.08 × 0.09
space group	$P2_12_12$
cell dimen	
temp (°C)	−137
a (Å)	20.833 (9)
b (Å)	20.368 (11)
c (Å)	9.702 (3)
Z (molecules/cell)	4
V (Å^3)	4116.77
D(calcd) (g/cm^3)	1.906
wavelength (Å)	0.710 69
mol wt	1181.29
linear absn coeff (cm^{-1})	87.156
detector to sample dist (cm)	22.5
sample to source dist (cm)	23.5
takeoff angle (deg)	2.0
av σ-scan width at half-height	0.25
scan speed (deg/min)	6.0
scan width (deg dispersion)	1.8
individual background (s)	6
aperature size (mm)	3.0 × 4.0
2θ range (deg)	6–45
total no. of reflctns collected	3163
no. of unique intensities	3041
no. of $F > 0.0$	2886
no. of $F > 3.0\sigma(F)$	2644
$R(F)$	0.0504
$R_w(F)$	0.0471
goodness of fit for the last cycle	0.846
max δ/σ for last cycle	0.05

$W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}CMe)(Cl)_2$. (a) $W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}CMe)$ (0.1 g, 0.09 mmol) was dissolved in hexane (4 mL) to give a dark brown solution, and $(PhCN)_2PdCl_2$ (0.06 g, 0.16 mmol) was added. The solution quickly turned dark green and Pd metal precipitated. The mixture was stirred at ambient temperature for 20 min and filtered, and the volatiles were removed from the filtrate in vacuo. Fresh hexane (ca. 1 mL) was added and the solution cooled to −15 °C for 2 days to provide 64 mg (60% yield) of 1 as dark green crystals. (b) $W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}CMe)$ (0.29 g, 0.26 mmol) was dissolved in hexane (10 mL) to give a dark brown solution, and C_2Cl_6 (0.062 g, 0.26 mmol) was added. The solution immediately turned dark green, and after the solution was stirred for 15 min the volatiles were removed in vacuo. Fresh hexane (ca. 1 mL) was added and the solution cooled to −15 °C overnight to provide 135 mg (45% yield) of 1 as dark green crystals.

^1H NMR (toluene-d_8, 22 °C): OC*H*Me$_2$, δ 6.48, 6.15, 5.87 (1, br), 5.54, 5.37 (2, br), 5.10 (1, br), 4.51 (1, septet); μ_3-C*Me*, δ 4.74 (3, s); a complex set of broad, overlapping resonances are observed between 1.90 and 0.45 ppm for the OCH*Me*$_2$ groups. ^1H NMR (toluene-d_8, −20 °C): OC*H*Me$_2$, δ 6.48, 6.18, 5.94, 5.61, 5.53, 5.47, 5.34, 5.13, 4.45 (1, septets); μ_3-C*Me*, δ 4.76 (3, s); 18 doublets (some overlapping) are observed between 1.90 and 0.50 for the OCH*Me*$_2$ groups. $^{13}C\{^1H\}$ NMR (toluene-d_8, −70 °C): μ_3-*C*Me, δ 302.3; O*C*HMe$_2$, δ 86.0, 85.2, 82.1, 81.8, 81.7, 81.3, 80.8, 78.0, 77.6; μ_3-C*Me*, δ 35.5; 17 separate signals are observed between 28.7 and 22.8 ppm for the OCH*Me*$_2$ groups. $W_3(O\text{-}i\text{-}Pr)_9(\mu_3\text{-}^{13}CMe)(Cl)_2$: $^{13}C\{^1H\}$ NMR (toluene-d_8, −20 °C) δ 303.3 ($^1J_{^{183}W-^{13}C}$ = 117.5, 98.8, 47.7 Hz; I = 11.7%, 12.3%, 14.1%); $^{13}C\{^1H\}$ NMR (toluene-d_8, 22 °C) δ 304.1 ($^1J_{^{183}W-^{13}C}$ = 117.4, 79 Hz; I = 12.4%, 21.9%); $^{13}C\{^1H\}$ NMR (toluene-d_8, 37 °C) δ 304.8 ($^1J_{^{183}W-^{13}C}$ = 117.3, 75.5 Hz; I = 11.5%, 20.7%).

IR (cm^{-1}): 2965 (s), 2920 (m), 1461 (w), 1448 (w), 1373 (m), 1365 (m), 1339 (w), 1318 (m), 1262 (w), 1166 (m), 1110 (s), 990 (s), 970 (s), 850 (s), 815 (m), 604 (m), 466 (m), 380 (w).

Anal. Calcd for $C_{29}H_{66}Cl_2O_9W_3$: C, 29.49; H, 5.59; Cl, 6.00. Found: C, 29.55; H, 5.49; Cl, 6.17.

Reactions with $HgCl_2$ and $(PhCN)_2PtCl_2$. Reactions between $W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9$ and each of $HgCl_2$ and $(PhCN)_2PtCl_2$ carried in NMR tubes in benzene-d_6 were found to generate I as shown by ^1H NMR.

Crystallographic Studies. General operating procedures and listings of programs have been previously given.[9]

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(7) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

(8) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1984**, *23*, 4476.

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A small almost cubic crystal of 0.08 mm on the side was selected under inert-atmosphere conditions. The crystal was transferred to the goniostat where it was cooled to −137 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited orthorhombic symmetry and systematic extinction of $h00$ for $h = 2n + 1$ and of $0k0$ for $k = 2n + 1$, uniquely identifying the space group as the noncentrosymmetric $P2_12_12$. Data were collected in the manner detailed in Table III. A total of 3163 reflections were collected; after the usual data processing and averaging of equivalent reflections a unique set of 3041 reflections remained. A total of 2644 reflections considered observed by the criterion $F > 3.0\sigma(F)$ were used in the final least-squares refinement of the structure.

The structure was solved by a combination of direct methods and heavy-atom Fourier techniques. All non-hydrogen atoms were readily located. Initial full-matrix least-squares refinement leads to an R of 0.059. Since the space group is noncentrosymmetric, the other enantiomer was tested, the R was 0.054, and the refinement was continued by using this enantiomer. The least-squares refinement was completed by using anisotropic thermal parameters on all W and Cl atoms, while the C and O atoms were isotropic. Hydrogen atoms were introduced in calculated fixed positions on all of the C atoms in the OR groups. A difference map showed the position of two of the hydrogen atoms on C(43), and the third one was calculated. The final R was 0.050 for 2644 reflections.

The final difference Fourier was essentially featureless. The maximum peak was 1.5 e/Å^3, and several peaks of approximately 1.2–1.5 e/Å^3 were located in close proximity to the heavy atoms. No absorption correction was deemed necessary due to the almost cubic shape of the crystal.

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Registry No. 1, 113220-80-7; A, 92054-28-9; $(PhCn)_2PdCl_2$, 14220-64-5; $(PhCN)_2PtCl_2$, 14873-63-3; C_2Cl_6, 67-72-1; $HgCl_2$, 7487-94-7; W, 7440-33-7.

Supplementary Material Available: Tables of calculated H-atom positions, anisotropic thermal parameters, and complete bond distances and angles and alternate ball-and-stick drawings (9 pages); a listing of F_o and F_c values (7 pages). Ordering information is given on any current masthead page.

How Dioxygen Activates C–H Bonds of Simple Arenes in Unstable CpFe^I(arene) Complexes and the Versatile Reactivity of Superoxide Anion Generated from Dioxygen and Organoiron "Electron Reservoirs"[1]

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The reactivity of $O_2^{\bullet-}$ generated in inert solvents and ethers from dioxygen and electron reservoirs such as CpFe^I(arene) complexes has been examined with the aim of activating benzylic C–H bonds in simple arenes coordinated to CpFe^I. The C–H activation by O_2 in pentane, THF, or DME, known for $C_5R_5Fe^I(C_6R'_6)$ (R and R′ = alkyls), is investigated for unstable CpFe^I(arene) complexes with one to six methyl groups on the arene ligand. A dramatic salt effect is found when the reactions are carried out in THF; in the presence of Na^+X^-, the formation of yellow diagmagnetic salts $[CpFe(arene)]^+X^-$ and of $^1/_2$ mol of Na_2O_2 is general; it is quantitative with $X^- = PF_6^-$ upon reaction with $^1/_2$ mol of O_2 at −80 °C. When Na^+X^- is removed, the unstable CpFe^{II}(η^5-benzyl) complexes are obtained in high yield and characterized by the downfield resonance (140 ppm) observed in the $^{13}C\{^1H\}$ spectra for the ring carbon bound to the exocyclic double bond; they can be alkylated or functionalized in situ at −50 °C with CH_3I or PhCOCl. Primary, secondary, and tertiary C–H bonds can be activated in this way by O_2 in the 19-electron CpFe^I(arene) complexes. The rapid H-atom abstraction from methyl and ethyl substitutents at −80 °C is an outer-sphere electron transfer to dioxygen followed by deprotonation by superoxide anion, the latter process being inhibited by the salt effect (Na^+). The formation of dimeric peroxides is a general phenomenon in the reactions of $^1/_2$ mol of O_2 in pentane or toluene with CpFe^I complexes of arenes such as C_6H_6 or 1,3,5-t-$Bu_3C_6H_3$ which do not bear benzylic hydrogens. The competition between formation of a dimeric peroxide and benzylic H abstraction is exemplified by the behavior of CpFe^I(i-PrC_6H_5); reaction of O_2 with the latter in toluene gives the dimeric peroxide as the kinetic product (−80 °C), transformed into the thermodynamic H abstraction product at −17 °C. The salt effect in THF with M^+X^- (M^+ = n-Bu_4N^+, K^+, Na^+, $X^- = PF_6^-$, BF_4^-, F^-) also inhibits the formation of dimeric peroxide, and the salts $[CpFe(arene)]PF_6$ and Na_2O_2 are formed instead of the dimer. The salt effect is all the more important in the series M^+X^- as the size of the cation M^+ decreases and as that of the anion X^- increases. In all the reactions, formation of superoxide anion in ion pairs is the first step and its versatile reactivity (proton abstraction, nucleophilic addition, reduction or dismutation) accounts for the variety of reactions observed.

Introduction

The reactivity of superoxide radical anion has recently attracted considerable attention from chemists[2-8] and biochemists.[9,10] Some years ago it was reported[11,12] that the reactions of the stable 19-electron complexes CpFe^I(C_6R_6) (R = Me, Et) with O_2 formally give H-atom ab-

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