7 and 55 mg (0.19 mmol) of the iron cyclooctatriene complex. Workup as before gave 9 mg of product, corresponding to ca. 10% yield. Exact mass: calcd for $^{56}Fe_3{}^{12}C_{50}{}^{11}B_{10}{}^{1}H_{86}{}^{+}$, 964.5708; found, 964.5714.

Synthesis of *p*-[(MeC$_6$H$_4$CHMe$_2$)Ru(2,3-Et$_2$C$_2$B$_3$H$_4$-5-CH$_2$)]$_2$(C$_6$H$_4$)Fe(Et$_2$C$_2$B$_4$H$_4$) (12). The procedure employed in the synthesis of 9 and 11 was followed with use of 83 mg (0.10 mmol) of 8 and 60 mg (0.21 mmol) of the iron cyclooctatriene complex. The reaction was conducted at 150 °C for 30 min followed by 180 °C for 90 min. Workup as described above gave 22 mg (0.02 mmol, 22%) of brown solid **12**. The unit-resolution mass spectrum of 12 exhibits a broad parent ion envelope between *m/z* 1005 and 988 that closely matches the intensity pattern calculated from natural isotope distributions, with the high-mass peak corresponding to $^{104}Ru_2{}^{56}Fe^{13}C^{12}C_{45}{}^{11}B_{10}{}^{1}H_{78}{}^{+}$). Major fragments appear at P − 130 (loss of $Et_2C_2B_4H_4$) and P − 186 (loss of $Fe(Et_2C_2B_4H_4)$).

Acknowledgment. We thank Dr. Mike Kinter for the high-resolution mass spectra and Kevin Chase for several of the boron NMR spectra. The support of the National Science Foundation (Grant No. CHE 87-21657) and the U.S. Army Research Office is gratefully acknowledged.

Monodemethylation of a Coordinated Ditelluroether. Synthesis and X-ray Structure of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$]

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When [Pd{*o*-C$_6$H$_4$(TeMe)$_2$}I$_2$] is heated for short periods in dimethyl sulfoxide or the solution allowed to stand for several days at room temperature, monodemethylation occurs with the formation of the title complex, the structure of which was established by a single-crystal X-ray study. Crystal data for [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$] at room temperature: monoclinic, a = 11.142 (2) Å, b = 20.785 (2) Å, c = 19.596 (4) Å, β = 92.66 (2)°, Z = 4, space group $P2_1/n$, and R_w = 0.045 for 4467 data ($F > 3\sigma(F)$). The structure is based on a tetrameric unit containing an eight-membered ring (Pd$_4$Te$_4$) in which each square-planar-coordinated Pd atom is surrounded by one I and three Te atoms. The Te atom that does not have a methyl group attached is bonded to two Pd atoms and is part of the ring. Some spectroscopic properties of the title complex are reported and discussed. Realkylation does not occur on treatment of the tetramer with MeI.

Introduction

S-Dealkylation of metal-coordinated thioether groups has been observed in many systems,[1] the first report of such a process being over 100 years ago.[2] Detailed investigations have been carried out on a number of nickel(II), palladium(II), and platinum(II) systems, including those with the ligands *o*-C$_6$H$_4$(AsMe$_2$)(SMe),[3] PhP(*o*-C$_6$H$_4$SMe)$_2$,[4] *o*-C$_6$H$_4$(PPh$_2$)(SMe), and *o*-C$_6$F$_4$(PPh$_2$)(SMe),[5] the dealkylation occurring upon heating the complex in a high-boiling solvent such as *N*,*N*-dimethylformamide or dimethyl sulfoxide (DMSO) and being promoted by the addition of nucleophiles such as I$^-$ and CNS$^-$. Mechanistically the dealkylation is thought to be similar to Zeisel ether cleavage,[5,6] and the reaction can often (but not always) be reversed by treatment of the resulting thiolate complex with alkylating agents.[1–7] Similar Se-dealkylation of coordinated selenoether functions has been reported.[6,8] Dealkylation of coordinated dithio-[9] and diselenoethers[10] occurs either on pyrolysis or on heating in DMSO solution, but the reactions are complicated by the presence of several potential sites of R–S(Se) bond cleavage. Much less is known about tellurium ligands,[11] and chelating bidentate telluroether complexes have been reported only recently.[12,13] Complexes of telluride (RTe$^-$) groups have been prepared from RTeTeR or NaTeR and suitable metal substrates,[14] and the complex [Pt(PPh$_3$)$_2$(*o*-C$_6$H$_4$Te$_2$)] has been structurally characterized.[15] Here we report the first example of monodealkylation of a coordinated ditelluroether and the structure of the unusual tetrameric product.

Experimental Section

Physical measurements were made as described previously.[12,13]

Preparation of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$]. [Pd{*o*-C$_6$H$_4$(TeMe)$_2$}I$_2$][13] (0.1 g) was dissolved in DMSO (5 cm^3) and heated on a water bath for 3 h. A black solid separated out over this period. This was filtered off, washed with DMSO and diethyl ether, and dried in vacuo; yield 0.065 g, 81%. Anal. Calcd for C$_{28}$H$_{28}$I$_4$Pd$_4$Te$_8$: C, 14.5; H, 1.2. Found: C, 14.2; H, 1.2.

X-ray Structure Analysis. Dark, air-stable, rectangular plates of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$] were obtained during an attempt to obtain the ditelluroether complex from DMSO solution

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Table I. Crystal Data and Data Collection Details

molecular formula	$C_{28}H_{28}I_4Pd_4Te_8$
fw	2318.5
space group	monoclinic, $P2_1/n$ (No. 14)
a, Å	11.142 (2)
b, Å	20.785 (2)
c, Å	19.596 (4)
β, deg	92.66 (2)
V, Å^3	4533.3
Z	4
d(obsd),[a] g cm^{-3}	3.30 (3)
d(calcd), g cm^{-3}	3.396
F(000), e	4032
radiatn	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	93.1
2θ range, deg	3.0–50.0
total no. of data	8810
total no. of unique data	7958 (R_{int} = 0.006)
no. of obsd. data ($F > 3\sigma(F)$)	4467
no. of params	210
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
max shift/error in final cycle	0.16
residual electron dens, e Å^{-3}	1.60
R	0.055
R_w	0.045
GOF	1.48

[a] Obtained by the flotation method in $CH_2I_2/CHCl_3$.

Table II. Atomic Coordinates and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U[a]
Pd(1)	0.23248 (11)	0.30705 (7)	1.13025 (6)	37.7 (8)*
Pd(2)	−0.08029 (11)	0.18851 (8)	1.12079 (6)	39.6 (8)*
Pd(3)	0.24157 (11)	0.18996 (7)	1.01178 (6)	36.2 (8)*
Pd(4)	−0.08117 (11)	0.30517 (8)	1.00792 (6)	38.4 (8)*
I(1)	0.38917 (11)	0.39837 (7)	1.09773 (7)	54.1 (8)*
I(2)	−0.24008 (11)	0.21611 (8)	1.21311 (6)	60.4 (9)*
I(3)	0.39473 (12)	0.09487 (7)	1.04324 (8)	64.8 (9)*
I(4)	−0.23892 (11)	0.26753 (7)	0.91011 (6)	50.7 (8)*
Te(1)	0.40975 (10)	0.23891 (7)	1.17280 (5)	45.9 (7)*
Te(2)	0.09101 (10)	0.23992 (6)	1.19741 (5)	41.2 (7)*
Te(3)	−0.25343 (10)	0.14142 (7)	1.04729 (6)	47.9 (8)*
Te(4)	0.06675 (10)	0.12212 (7)	1.05689 (6)	42.1 (7)*
Te(5)	0.41742 (10)	0.25520 (6)	0.96927 (5)	39.1 (7)*
Te(6)	0.09630 (09)	0.25807 (6)	0.94152 (5)	37.9 (7)*
Te(7)	−0.26280 (10)	0.34522 (7)	1.06931 (6)	45.2 (8)*
Te(8)	0.05464 (10)	0.37652 (7)	1.08128 (6)	42.8 (7)*
C(1)	0.4643 (17)	0.2942 (10)	1.2626 (9)	54 (5)
C(2)	−0.2779 (23)	0.0551 (13)	1.1039 (11)	88 (8)
C(3)	0.4428 (20)	0.2006 (12)	0.8777 (10)	72 (6)
C(4)	−0.2915 (19)	0.4325 (11)	1.0122 (9)	64 (6)
C(11)	0.3255 (10)	0.1644 (5)	1.2256 (5)	44 (4)
C(12)	0.2007 (10)	0.1616 (5)	1.2287 (5)	45 (4)
C(13)	0.1474 (10)	0.1107 (5)	1.2626 (5)	66 (6)
C(14)	0.2188 (10)	0.0627 (5)	1.2933 (5)	75 (7)
C(15)	0.3435 (10)	0.0655 (5)	1.2901 (5)	75 (6)
C(16)	0.3968 (10)	0.1164 (5)	1.2563 (5)	60 (5)
C(21)	−0.1627 (10)	0.0984 (6)	0.9666 (5)	50 (5)
C(22)	−0.0375 (10)	0.0977 (6)	0.9664 (5)	45 (5)
C(23)	0.0199 (10)	0.0734 (6)	0.9102 (5)	59 (6)
C(24)	−0.0479 (10)	0.0496 (6)	0.8541 (5)	76 (7)
C(25)	−0.1731 (10)	0.0503 (6)	0.8542 (5)	86 (7)
C(26)	−0.2305 (10)	0.0746 (6)	0.9104 (5)	77 (7)
C(31)	0.3277 (10)	0.3320 (5)	0.9191 (5)	45 (4)
C(32)	0.2028 (10)	0.3376 (5)	0.9152 (5)	44 (4)
C(33)	0.1487 (10)	0.3913 (5)	0.8841 (5)	55 (5)
C(34)	0.2194 (10)	0.4393 (5)	0.8568 (5)	74 (6)
C(35)	0.3443 (10)	0.4338 (5)	0.8606 (5)	77 (7)
C(36)	0.3985 (10)	0.3801 (5)	0.8918 (5)	59 (5)
C(41)	−0.1795 (10)	0.3881 (6)	1.1579 (5)	52 (5)
C(42)	−0.0549 (10)	0.3947 (6)	1.1653 (5)	41 (4)
C(43)	−0.0022 (10)	0.4179 (6)	1.2264 (5)	58 (6)
C(44)	−0.0740 (10)	0.4345 (6)	1.2801 (5)	53 (5)
C(45)	−0.1985 (10)	0.4279 (6)	1.2728 (5)	74 (6)
C(46)	−0.2512 (10)	0.4047 (6)	1.2117 (5)	61 (6)

[a] Asterisks denote equivalent isotropic temperature factors from anisotropic atoms (U_{eq} = $^1/_3$(trace of orthogonalized U)).

by vapor diffusion of diethyl ether. The crystals were visually of poor quality and were sealed in thin-wall glass capillaries. Several crystals were examined by photographic X-ray diffraction methods, and all appeared to be the same compound. With use of an Enraf-Nonius CAD4 diffractometer fitted with a graphite monochromator and Mo radiation, a room-temperature crystal (ca. 0.3 × 0.05 × 0.2 mm) was used to determine accurate cell dimensions from 25 carefully centered reflections and subsequently used for the data collection. The two check reflections showed no decay during the experiment, and an empirical ψ-scan absorption correction was applied to the data (transmission minimum 40.3% and maximum 99.8%). The systematic absences established the space group, and the structure was solved with use of SHELXS-86[16] (TREF), which yielded six possible low CFOM solutions, one of which developed a satisfactory if unexpected chemical model. Structure factor calculations and difference electron density syntheses located carbon atoms, and later maps showed evidence for H atoms, which were introduced into the model in calculated positions (C–H = 0.95 Å). Full-matrix least-squares refinement with anisotropic (Pd, Te, I) and isotropic (C, H) atoms and rigid phenyl groups (C–C = 1.395 Å) converged to R = 0.055. Further details are given in Table I, and atomic coordinates are listed in Table II. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX-76[17] (C, H) and ref 18 (Pd, Te, I), and all calculations were performed on an IBM 3090 computer using the programs SHELXS-86,[16] SHELX-76,[17] ORTEP,[19] and XANADU.[20]

Results and Discussion

Synthesis. A small number of brown-black crystals of the title complex were obtained adventitiously during attempts to grow crystals of [Pd{o-C_6H_4(TeMe)$_2$}I_2][13] from a DMSO solution by vapor diffusion of diethyl ether. Their identity was subsequently established by an X-ray study. Conditions for a rational synthesis were established by heating a solution of the diiodide complex in DMSO-d_6 for varying periods of time and monitoring the changes by ^{1}H NMR spectroscopy. The proton NMR resonances of the diiodide δ(Me) at 2.70 and 2.68 ppm (due to the meso and DL invertomers)[13] decreased in intensity with time, and new resonances appeared, including a singlet at 2.66 ppm assigned to the MeTe group of the monodealkylated complex. A peak at 2.17 ppm was assigned to MeI by comparison with the spectrum of a genuine sample; other resonances at 3.96, 2.99, and 2.24 ppm remain unassigned and probably result from side reactions involving the solvent. A ^{125}Te{^{1}H} NMR spectrum of one of the mixtures revealed only the resonances of the starting material and of the dealkylated complex (below), showing that no other tellurium-containing species were formed in significant amounts. On the basis of these results the complex [{Pd(*o*-C_6H_4(TeMe)Te)I}$_4$] was prepared by heating [Pd{*o*-C_6H_4(TeMe)$_2$}I_2] in DMSO for 3 h at 100 °C. It is a brown-black solid readily distinguishable from the red-brown diiodide.

Structure of [{Pd(*o*-C_6H_4(TeMe)Te)I}$_4$]. The structure consists of discrete tetrameric units with each palladium surrounded in an approximately square-planar arrangement by three tellurium atoms and one iodine atom. The tetrameric structure arises from palladium atoms

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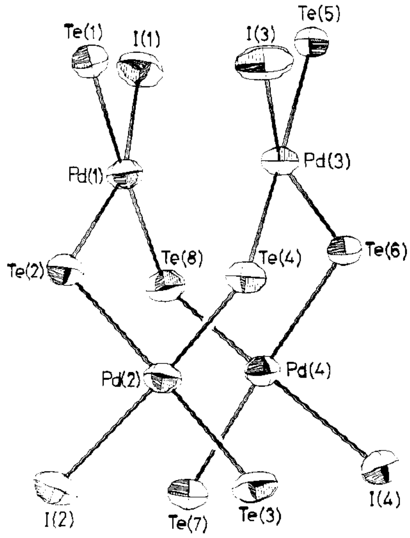

Figure 1. The heavy-atom framework showing Pd, I, and Te atoms involved in the tetrameric unit. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

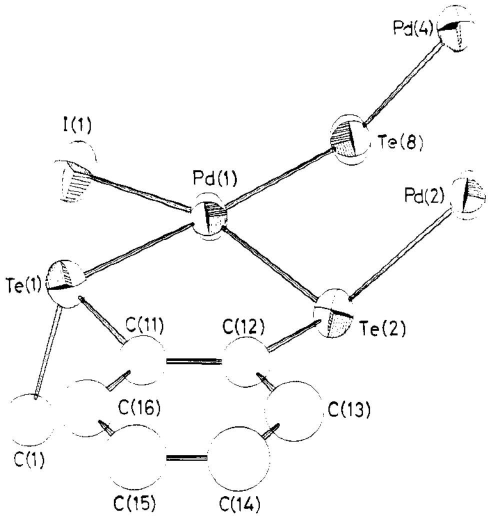

Figure 2. Environment around Pd(1) showing the atom-labeling scheme and excluding H atoms for clarity. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

being bridged by demethylated tellurium atoms, and the resulting eight-membered ring (Pd_4Te_4), which is similar to the "cradle" geometry of S_4N_4, is shown in Figure 1. The molecule has no crystallographic symmetry but is approximately S_4. The two shortest Pd···Pd distances (Pd(1)···Pd(3) = 3.368 (2) Å, Pd(2)···Pd(4) = 3.282 (2) Å) are regarded as nonbonding by comparison with the Pd···Pd distances in [Pd(en)Cl_2] (3.37 Å), for which spectroscopic studies indicated no interaction.[21] The three Pd–Te distances around every Pd atom fall into three classes (see Table III): the middle value (2.55 Å) is the bond to the methylated Te atom, the shortest (2.52 Å) is the bond to the demethylated Te atom there by virtue of the ligand carbon framework, and the longest (2.60 Å) is the remaining Pd to demethylated Te atom distance. Thus, in Figure 2, Pd(1)–Te(2) is the shortest (2.521 (2) Å) and Pd(1)–Te(8) the longest distance (2.599 (2) Å), and the Te bridge bonds are unsymmetrical. As expected, the Te atom coordination is approximately pyramidal with bond angles in the range 95–115°. The coordination around Pd(1) is shown in Figure 2, and the other three Pd atoms are very similar. The planar six-membered carbon ring and the two directly bonded Te atoms are approximately coplanar (δ|Te–C–C–Te| = 12° (average)). The "bite" of the ditellurium ligand is 3.59 Å (average), which is only a little shorter than the shortest interligand distance (Te(4)···Te(6) = 3.643 (2) Å). In principle there are a number of possible stereoisomers depending on the methyl position. However, including carbon atoms, the tetrameric unit still retains approximately S_4 symmetry, and under this point group, all the methyl C atoms would be equivalent with the methyl groups pointing away from the Pd_4Te_4 ring.

Table III. Selected Bond Distances (Å) and Bond Angles (deg)

Pd(1)–I(1)	2.676 (2)	Pd(3)–I(3)	2.665 (2)
Pd(2)–I(2)	2.659 (2)	Pd(4)–I(4)	2.657 (2)
Pd(1)–Te(1)	2.540 (2)	Pd(3)–Te(4)	2.593 (2)
Pd(1)–Te(2)	2.521 (2)	Pd(3)–Te(5)	2.554 (2)
Pd(1)–Te(8)	2.599 (2)	Pd(3)–Te(6)	2.513 (2)
Pd(2)–Te(2)	2.602 (2)	Pd(4)–Te(6)	2.608 (2)
Pd(2)–Te(3)	2.549 (2)	Pd(4)–Te(7)	2.542 (2)
Pd(2)–Te(4)	2.519 (2)	Pd(4)–Te(8)	2.521 (2)
Te–C(methyl)	2.13 (3)–2.16 (2)	C–C(fixed)	1.395
Te–C(aryl)	2.104 (9)–2.135 (12)	C–H(fixed)	0.95
I(1)–Pd(1)–Te(1)	88.1 (1)	I(3)–Pd(3)–Te(4)	90.1 (1)
I(1)–Pd(1)–Te(2)	161.4 (1)	I(3)–Pd(3)–Te(5)	88.7 (1)
I(1)–Pd(1)–Te(8)	90.7 (1)	I(3)–Pd(3)–Te(6)	159.1 (1)
Te(1)–Pd(1)–Te(2)	90.9 (1)	Te(4)–Pd(3)–Te(5)	178.6 (1)
Te(1)–Pd(1)–Te(8)	177.5 (1)	Te(4)–Pd(3)–Te(6)	91.0 (1)
Te(2)–Pd(1)–Te(8)	90.9 (1)	Te(5)–Pd(3)–Te(6)	90.4 (1)
I(2)–Pd(2)–Te(2)	90.9 (1)	I(4)–Pd(4)–Te(6)	91.2 (1)
I(2)–Pd(2)–Te(3)	87.4 (1)	I(4)–Pd(4)–Te(7)	85.6 (1)
I(2)–Pd(2)–Te(4)	158.1 (1)	I(4)–Pd(4)–Te(8)	160.7 (1)
Te(2)–Pd(2)–Te(3)	177.8 (1)	Te(6)–Pd(4)–Te(7)	176.2 (1)
Te(2)–Pd(2)–Te(4)	92.0 (1)	Te(6)–Pd(4)–Te(8)	93.2 (1)
Te(3)–Pd(2)–Te(4)	90.1 (1)	Te(7)–Pd(4)–Te(8)	90.4 (1)
Pd(1)–Te(2)–Pd(2)	112.7 (1)	Pd(3)–Te(6)–Pd(4)	115.0 (1)
Pd(2)–Te(4)–Pd(3)	112.8 (1)	Pd(4)–Te(8)–Pd(1)	108.1 (1)
Te(1)···Te(2)	3.606 (2)	Te(5)···Te(6)	3.594 (2)
Te(3)···Te(4)	3.586 (2)	Te(7)···Te(8)	3.593 (2)
Pd···Pd (min)	3.282 (2)		
Te···Te (between different ligands (min))	3.643 (2)		

The Pd–I distances (2.664 Å (average)) may be compared with those in monomeric [Pd{o-$C_6H_4(PPh_2)$(SMe)}I_2],[22] where the difference in bond lengths was associated with the trans influence of P > S. This would make RTe^- comparable to P in this sequence. Similar Pd–Te distances have been reported[12] in [Pd{*meso*-PhTe$(CH_2)_3$TePh}Br_2] (2.526 Å (average)).

Demethylation of sulfur[8,23,24] and selenium[6] in complexes of bidentate chelating ligands has been characterized by X-ray diffraction, and in the case of [Pd{o-$C_6H_4(PPh_2)$(S)}I]$_2$,[8] dimeric units were found rather than the tetrameric species reported here.

Properties. The tetramer is poorly soluble in all common solvents, including DMSO, and this hindered NMR studies in particular. The UV–visible spectrum of the tetramer is easily distinguished from that of the diiodide (Figure 3), the lowest energy absorption shifting to higher energy by ca. 3000 cm^{-1} between the Te_2I_2 and Te_3I donor sets. The $^{125}Te\{^1H\}$ NMR spectrum consists of two signals in approximately 1:1 intensity at 688 and 427 ppm (relative to neat external Me_2Te, δ = 0). The o-C_6H_4(TeMe)Te^- ligand was generated in situ in the present complex and is presently unknown in the free state. The ^{125}Te chemical

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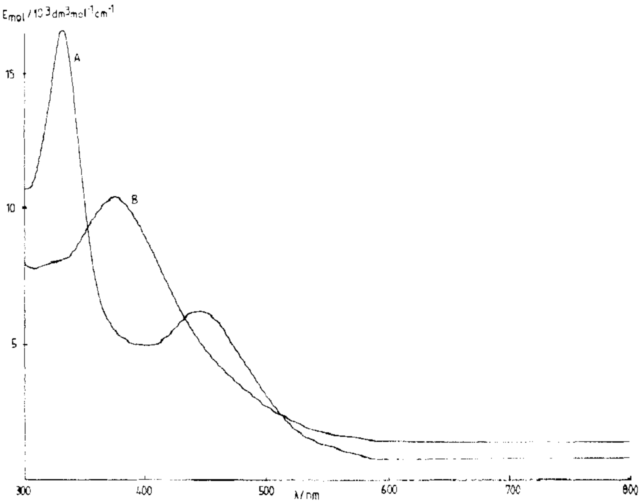

Figure 3. UV-Visible spectra of $[Pd\{o\text{-}C_6H_4(TeMe)_2\}I_2]$ (A) and $[\{Pd(o\text{-}C_6H_4(TeMe)Te)I\}_4]$ (B) in DMSO solution.

shifts in ortho-substituted telluroethers $o\text{-}C_6H_4(TeMe)(R)$ (R = H, OMe, NMe_2, Cl, PMe_2, etc.)[25,26] lie in the range 200–375 ppm, and thus the resonance of the TeMe group in free $o\text{-}C_6H_4(TeMe)Te^-$ is expected to lie in (or near) this range. Bildstein et al.[27] have reported ^{125}Te chemical shifts for a variety of telluride anions in $Li^+[o\text{-}C_6H_4Te(R)]^-$ which lie to low frequency of those of $TeMe_2$ (−229 to −13 ppm). From comparisons of the chemical shifts in the pairs $o\text{-}C_6H_4(OMe)(TeMe)/o\text{-}C_6H_4(OMe)Te^-$ (+206/−229 ppm), $o\text{-}C_6H_4(NMe_2)(TeMe)/o\text{-}C_6H_4(NMe_2)Te^-$ (+236/−211 ppm), and $PhTeMe/PhTe^-$ (+329/−122 ppm), it appears that the chemical shifts of the tellurides lie approximately 450 ppm to low frequency from those of the corresponding telluroethers. Hence, from $o\text{-}C_6H_4(TeMe)_2$ (δ = 372)[26] we can estimate the shift of the telluride group in $o\text{-}C_6H_4(TeMe)Te^-$ as −80 ± 50 ppm. When the ligand is coordinated to a metal, a large high-frequency shift is expected, due both to electron donation to the metal and to the presence of a five-membered chelate ring.[13] The presence of only one resonance for Te(Me) and one for Te^- in the tetramer (and of the single ^{1}H NMR TeMe resonance), indicate that only one environment is present for each, whereas several stereoisomers are possible. This could be due to fast inversion on the NMR time scale or to the presence of only one isomer in significant amounts. Unfortunately the very poor solubility prevents a variable-temperature NMR study to investigate this matter further (even at ambient temperature the ^{125}Te data required ca. 400 000 transients for an adequate signal to noise ratio to be achieved).

Attempts to realkylate the title complex by treatment with excess MeI in CH_2Cl_2 or ethanol were unsuccessful.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atomic coordinates, and full bond length and bond angle data (4 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the Chiral Rhenium Phenyl Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$

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Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ and C_6H_5Cu gives chiral, racemic phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1, 82–92%), which undergoes a spontaneous resolution when crystallized from CH_2Cl_2/hexanes. The crystal structure (monoclinic, $P2_1$, a = 9.261 (2) Å, b = 14.142 (3) Å, c = 10.722 (2) Å, β = 112.74 (1)°, Z = 2) exhibits an unexpected $Re\text{-}C_\alpha$ conformation that places one ortho carbon in the region between the nitrosyl and PPh_3 ligands. Reaction of 1 and $HBF_4 \cdot O(C_2H_5)_2$ in CH_2Cl_2 at −80 °C gives, as the first species detected by NMR, η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (2). Between −70 and −40 °C, 2 converts to dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (3), even in the presence of excess benzene. Reaction of 1 and $Ph_3C^+PF_6^-$ in CH_2Cl_2 at −80 °C gives bis(vinyl)alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH{-}CH{=}CH{-}CH(CPh_3){-}CH{=}CH)]^+PF_6^-$ (7), which decomposes above −40 °C to 3 and other products that ultimately yield tetraphenylmethane.

Introduction

We have had an ongoing interest in the synthesis, structure, and reactivity of complexes of the chiral, electron-rich rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and unsaturated hydrocarbon fragments such as vinyls (—CH=CHR),[1] allyls (—CH_2CH=CHR),[2] alkylidenes (=CHR),[3] and alkenes (H_2C=CHR).[4] Many of these complexes undergo highly stereoselective reactions with

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