-40 °C, δ 222.4 (*CO*, vbr), 221.6 (*CO*), 100.5 [C(1), C₅H₄Me], 101.0 and 91.7 (br, 2 C each, C₅H₄Me), 12.4 (Me); -80 °C, 222.1 (W–*CO*, $^1J_{WC}$ = 156 Hz), 221.5 (W–*CO*, $^1J_{WC}$ = 179 Hz), 99.7 [C(1), C₅H₄Me], 101.4, 101.2, 91.55, 91.50 (1 C each, C₅H₄Me), 12.4 (Me). The 65 °C spectral parameters (benzene-d_6) were not significantly different from those recorded in acetone-d_6 at 20 °C. Anal. Calcd for C₂₇H₂₁O₉CoW₃: C, 29.48; H, 1.92. Found: C, 29.58; H, 1.76.

(ii) **Reaction of (OC)₄Co–Mo(CO)₃(η⁵-C₅H₄Me) (1a) with [W-(CO)₂(η⁵-C₅H₄Me)]₂ (W≡W).** 1a (178 mg, 0.30 mmol) and [W-(CO)₂(η⁵-C₅H₄Me)]₂ (W≡W) (191 mg, 0.30 mmol) were dissolved in toluene (20 mL) in a Schlenk tube equipped with a magnetic flea and capped with a rubber septum. The red solution did not change color when kept for ≈1.5 h at 25 °C under a fast nitrogen purge, so the reaction mixture was heated and maintained at 55 °C for a further 6 h, turning purplish black during this period. The solvent was then removed, the residue was dissolved in a ether/hexanes/dichloromethane mixture (2:1:1), and the solution was subjected to chromatography on silica gel. Elution with hexanes (with increasing quantities of ether added slowly) afforded a red, a purple, and a green band. The red band was shown by IR and ¹H NMR spectroscopy to be a mixture of 1a, 1b, and MM′-(CO)₆(η⁵-C₅H₄Me)₂ (M–M′; M, M′ = Mo or W]; the green (third) solution subsequently afforded crystals of 2b (35 mg, ≈5%). The second solution contained a mixture of two complexes. It was pumped to dryness and redissolved in a ether/hexanes/dichloromethane mixture (5:10:1), and the solution was subjected to careful chromatography. Slow elution with hexanes afforded greenish blue and purple bands. Recrystallization from hexanes afforded 3′ (35 mg, 12%) and 3b (20 mg, 6%), respectively. Data for 3′ are as follows. ¹³C{¹H} NMR (ppm in chloroform-d_1 at 20 °C): δ 222.9 (Mo, W–*CO*'s), 103.9 [C(1), Mo–C₅H₄Me], 100.8 (2 C, C₅H₄Me), 100.5 [C(1), W–C₅H₄Me], 99.9 (2 C, C₅H₄Me), 99.8 (2 C, C₅H₄Me), 93.7 (2 C, C₅H₄Me), 91.2 (2 C, C₅H₄Me), 91.1 (2 C, C₅H₄Me), 12.6 (Mo–C₅H₄*Me*), 12.4 (W–C₅H₄*Me*). Anal. Calcd for C₂₇H₂₁O₉CoMoW₂: C, 32.04; H, 2.09. Found: C, 31.94; H, 1.99.

(iii) **Reaction of (OC)₄Co–W(CO)₃(η⁵-C₅H₄Me) (1b) with Co₂(CO)₈.** Co₂(CO)₈ (0.26 mmol; 1.2 mL of a 0.215 M toluene solution) was added to a solution of 1b (135 mg, 0.26 mmol) in toluene (15 mL). A metallic mirror deposited from the dark solution after 3-h reflux. The solvent was removed, the residue dissolved in a hexane/ether mixture (3:1), and the solution passed through a silica gel column. Co₂(CO)₈ eluted first (hexanes). A green band was eluted by using a hexanes/ether mixture, and the final (purple-brown) band was collected by using pure diethyl ether. Concentration and cooling to -20 °C afforded crystals from both solutions. Green crystals consisting of an approximately 1:1 mixture of Co₂W₂(μ₂-CO)₃(CO)₇(η⁵-C₅H₄Me)₂ (2b) and 4 were obtained from the second band (70 mg of 2b and 4). Crystals of Co₃W(μ₂-CO)₃(CO)₈-(η⁵-C₅H₄Me) (5b) were harvested from the final band (50 mg, 0.050 mmol, 19%). Data for 4 are as follows. MS: *m/e* 553, 581. Anal. Found: C, 33.58; H, 1.44. Data for 5b are as follows. MS: *m/e* 748

(M⁺) and peaks corresponding to (M – nCO)⁺, n = 1–9. Anal. Calcd for C₁₇H₇O₁₁Co₃W: C, 27.30; H, 0.94. Found: C, 27.44; H, 0.82.

(iv) **Reaction of (OC)₄Co–Mo(CO)₃(η⁵-C₅H₄Me) (1a) with Co₂(CO)₈.** 1a (230 mg, 0.54 mmol) was added to Co₂(CO)₈ (180 mg, 0.54 mmol) in toluene (20 mL). The red-brown solution was refluxed gently for 1 h, the now brown mixture was pumped to dryness and dissolved in a hexanes/ether mixture (1:1), and the solution was subjected to silica gel chromatography using hexanes as the initial eluting solvent. After the elution of Co₂(CO)₈ and traces of [Mo(CO)₃(η⁵-C₅H₄Me)]₂, a green and a red-brown band were recovered with addition of some ether. The green band was subsequently found to contain 2a and 4. While these two compounds could not be separated, data for pure 2a could be deduced from spectra of the mixture. The final red-brown band contained 5a, which was crystallized and recovered as purple black crystals. Anal. Calcd for 5a, C₁₇H₇O₁₁Co₃Mo: C, 30.94; H, 1.07. Found: C, 31.07; H, 1.03.

(v) **Reaction of [W(CO)₂(η⁵-C₅H₄Me)]₂ (W≡W) with Co₂(CO)₈.** Toluene (40 mL) was added to a mixture of [W(CO)₂(η⁵-C₅H₄Me)]₂ (350 mg, 0.55 mmol) and Co₂(CO)₈ (190 mg, 0.55 mmol) in a Schlenk tube equipped with a stirrer bar and a pierced septum cap. After being stirred for 6 h under a vigorous nitrogen purge, the dark brown solution was pumped to dryness. The residue was dissolved in a mixture of solvents, and the solution was subjected to silica gel chromatography. Three species eluted with hexanes. These were identified as unreacted Co₂(CO)₈, [W(CO)₃(η⁵-C₅H₄Me)]₂, and 1b. A green band eluted with the addition of diethyl ether to the hexanes. Concentration and cooling of the solution to -20 °C afforded crystals of Co₂W₂(μ₂-CO)₃(CO)₇-(η⁵-C₅H₄Me)₂ (2b) (85 mg, 0.091 mmol, 16.5%). The final product, Co₃W(μ₂-CO)₃(CO)₈(η⁵-C₅H₄Me) (5b) (15 mg, 0.015 mmol), eluted off the column with almost pure ether and was crystallized from hexanes.

(vi) **Attempted Reaction of CoW₃(CO)₉(η⁵-C₅H₄Me)₃ (3b) with CO.** 3b (15 mg, 0.014 mmol) was dissolved in dichloromethane (≈3 mL), and the solution was stirred for 1 day under a CO atmosphere. No changes in the solution IR spectrum were noted, so the dichloromethane was removed, toluene (5 mL) was added, and the solution was magnetically stirred under a CO atmosphere at 55–60 °C for several days. After vacuum removal of the toluene, a dichloromethane solution IR spectrum of the residue only revealed IR bands assignable to 3b: no new bands were noted.

Supplementary Material Available: Full tables of crystal data and data collection parameters, positional parameters for all atoms, anisotropic thermal parameters, bond lengths, and bond angles (16 pages); structure factor listings (13 pages). Ordering information is given on any current masthead page.

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Dirhenium Complexes Derived from the Ligand 2-Mercaptoquinoline (2-mqH). Structure of [Re₂Cl₃(μ-dppm)₂(2-mq)]PF₆ (dppm = Ph₂PCH₂PPh₂)

Phillip E. Fanwick, Ju-sheng Qi, and Richard A. Walton*

The triply bonded dirhenium complexes Re₂X₄(dppm)₂ (X = Cl, Br; dppm = Ph₂PCH₂PPh₂) react with 2-mercaptoquinoline (2-mqH) to afford the 1:1 adducts Re₂X₄(dppm)₂(2-mqH), in which the 2-mqH ligand (in its zwitterionic form) is probably bound in a monodentate fashion through its deprotonated thiol donor. These complexes undergo a reversible one-electron transfer to give [Re₂X₄(dppm)₂(2-mqH)]⁺ (isolable as their PF₆⁻ salts). This oxidation is followed by the slow elimination of HX to give paramagnetic [Re₂X₃(μ-dppm)₂(2-mq)]PF₆, in which, in addition to two bridging dppm ligands, there is also a bridging 2-mq ligand bound through its N and S atoms. A single-crystal X-ray structure determination of the chloride complex has been carried out at 20 °C. Crystal data are as follows: monoclinic space group P2₁/c, a = 13.594 (3) Å, b = 20.185 (3) Å, c = 21.691 (4) Å, β = 104.459 (9)°, V = 5763 (3) Å³, Z = 4. The structure was refined to R = 0.030 (R_w = 0.037) for 5705 data with I > 3.0σ(I). The Re–Re distance is 2.2540 (5) Å, and the hydrogen atom on the carbon atom adjacent to the nitrogen of the quinoline ring forms a close contact with one of the rhenium atoms (the Re–H distance is 2.3 (1) Å). These compounds are the first multiply bonded dirhenium complexes that contain Re–thiol bonds.

Introduction

Multiply bonded dimetal complexes that contain bridging monoanionic ligands based upon bridging N–C–O⁻ and N–C–N⁻ units are well-known, whereas complexes that contain the corresponding N–C–S⁻ unit are comparatively rare.[1] Thus, in the

case of the quadruply bonded dimolybdenum(II) core, only the complexes Mo₂(dmmp)₄ (dmmpH = 4,6-dimethyl-2-mercapto-

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

pyrimidine),[2] $Mo_2(2\text{-mq})_4$ (2-mqH = 2-mercaptoquinoline),[3] and some isomeric species of the type $Mo_2[R_2PC(S)NR]_4$[4] are known that contain such N–C–S$^-$ units. To date, no such examples have been reported in the case of the related dirhenium chemistry.[5]

We are currently examining the chemistry of dirhenium complexes that contain sulfido or thiolato ligands and have included in our studies an investigation of the ability of such N–C–S$^-$ bridging ligands to stabilize the dirhenium core. In the present report we describe the isolation and characterization of the first such examples. A few preliminary details have been communicated previously.[3]

Experimental Section

The dirhenium(II) complexes $Re_2X_4(dppm)_2$ (X = Cl, Br) were prepared according to the reported method.[6] The 2-mercaptoquinoline ligand (2-mqH) was obtained from Eastman Kodak Co. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use, and all reactions were performed under an atmosphere of dry dinitrogen.

A. Reactions of $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with 2-Mercaptoquinoline in Acetone. (i) $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$. A mixture of $Re_2Cl_4(dppm)_2$ (0.22 g, 0.17 mmol) and 2-mqH (0.028 g, 0.17 mmol) in 10 mL of acetone was stirred at room temperature for 24 h. The dark purple-black precipitate that formed was filtered off, washed with a 10-mL portion of acetone, and then dried under vacuum; yield 0.25 g (95%). Anal. Calcd for $C_{62}H_{57}Cl_4NOP_4Re_2S$: C, 49.57; H, 3.82; Cl, 9.44. Found: C, 50.04; H, 4.37; Cl, 9.35. The IR spectrum of this product (Nujol mull) showed a $\nu(CO)$ mode for lattice acetone at 1710 cm^{-1}. This was further confirmed by ^1H NMR spectroscopy (in CD_2Cl_2), which revealed a resonance at δ +2.10 due to $(CH_3)_2CO$, showing the correct integration for the proposed stoichiometry.

Upon washing of the above complex with diethyl ether, the lattice acetone is lost and the composition of the product changes to $Re_2Cl_4(dppm)_2(2\text{-mqH})$. Anal. Calcd for $C_{59}H_{51}Cl_4NP_4Re_2S$: C, 49.07; H, 3.56; Cl, 9.82. Found: C, 49.09; H, 4.35; Cl, 10.19.

(ii) $Re_2Br_4(dppm)_2(2\text{-mqH})$. The procedure for the preparation of this complex from $Re_2Br_4(dppm)_2$ is analogous to that described in part A(i). This product was obtained as a dark purple-black precipitate and did not contain acetone of crystallization; yield 97%. Anal. Calcd for $C_{59}H_{51}Br_4NP_4Re_2S$: C, 43.69; H, 3.17; Br, 19.71. Found: C, 43.30; H, 3.50; Br, 19.55.

B. Oxidation of $Re_2X_4(dppm)_2(2\text{-mqH})$ with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. (i) $[Re_2Cl_4(dppm)_2(2\text{-mqH})]PF_6$. An equimolar mixture of $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$ (0.0504 g, 0.034 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.011 g, 0.034 mmol) in dichloromethane (10 mL) was stirred at room temperature for 10 min. The color of the reaction mixture changed from dark blue to purple. The solution was filtered into a large excess of diethyl ether (ca. 100 mL) with stirring. The resulting purple precipitate was filtered off, washed with diethyl ether (10 mL) and dried under vacuum; yield 0.0502 g (94%). Anal. Calcd for $C_{59}H_{51}Cl_4F_6NP_5Re_2S$: C, 44.59; H, 3.23; Cl, 8.92. Found: C, 44.68; H, 3.40; Cl, 8.31.

(ii) $[Re_2Br_4(dppm)_2(2\text{-mqH})]PF_6$. This complex was prepared from $Re_2Br_4(dppm)_2(2\text{-mqH})$ by a procedure analogous to that described in part B(i). It was obtained as a dark gray precipitate; yield 82%. Anal. Calcd for $C_{59}H_{51}Br_4F_6NP_5Re_2S$: C, 40.10; H, 2.91; Br, 18.09. Found: C, 40.52; H, 3.08; Br, 18.30.

(iii) $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$. The procedure for the preparation of this complex from $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$ was analogous to that described in part B(i) except that the reaction mixture was allowed to stir 5 days to ensure complete reaction. The product was obtained as a purple powder; yield 89%. Anal. Calcd for $C_{59}H_{50}Cl_3F_6NP_5Re_2S$: C, 45.64; H, 3.25; Cl, 6.85. Found: C, 46.46; H, 3.40; Cl, 5.92.

A similar reaction was carried out in acetone. The dark red solution that resulted was evaporated to dryness; the purple residue was then

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(6) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.

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Table I. Crystallographic Data for $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$

chem formula	$Re_2Cl_3SP_5F_6NC_{59}H_{50}$	Z	4
fw	1552.75	T, °C	20
space group	$P2_1/c$ (No. 14)	$\lambda(Mo\ K\alpha)$, Å	0.710 73
a, Å	13.594 (3)	ρ_{calcd}, g cm^{-3}	1.789
b, Å	20.185 (3)	$\mu(Mo\ K\alpha)$, cm^{-1}	46.24
c, Å	21.691 (4)	transm coeff	1.000–0.786
β, deg	104.459 (9)	R^a	0.030
V, Å^3	5763 (3)	R^b	0.037

$^a R = \sum ||F_o| - |F_c||/\sum |F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

washed with a 15-mL portion of diethyl ether and dried under vacuum; yield 0.056 g (73%).

(iv) $[Re_2Br_3(dppm)_2(2\text{-mq})]PF_6$. The procedure for preparation of this complex from $Re_2Br_4(dppm)_2(2\text{-mqH})$ was analogous to that described in part B(iii). It was obtained as a purple precipitate; yield 73%. The identity of this product was confirmed by cyclic voltammetry and ESR spectroscopy.

C. Reaction of $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$ with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). A mixture of $Re_2Cl_4(dppm)_2(2\text{-mqH})\cdot(CH_3)_2CO$ (0.074 g, 0.049 mmol) and approximately 1 equiv of DBU (0.0074 mL) in dichloromethane (10 mL) was stirred at room temperature for 1 day. The color of the reaction mixture changed from blue to green. The green solution was added to 100 mL of diethyl ether with stirring, and the green precipitate of $Re_2Cl_3(dppm)_2(2\text{-mq})$ that formed was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.045 g.

When this product was exposed to air, its color changed from green to purple as it oxidized to the paramagnetic cation $[Re_2Cl_3(dppm)_2(2\text{-mq})]^+$; the formation of the latter species was confirmed by cyclic voltammetry and ESR spectroscopy.

D. Bulk Electrolysis of $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$. A small quantity of this compound (0.02 g) was dissolved in 0.1 M $n\text{-Bu}_4NPF_6$–CH_2Cl_2 (20 mL) contained in an H-cell. Exhaustive electrolysis was performed on this solution at room temperature with the potential set at -0.40 V vs Ag/AgCl. The color of the solution changed from dark red-purple to green. Upon completion of the electrolysis, a cyclic voltammogram was recorded and found to be that of the reduced species $Re_2Cl_3(dppm)_2(2\text{-mq})$. ESR spectroscopy confirmed that reduction was essentially complete. The green species was quite unstable and easily reoxidized to the red cation when this solution was exposed to the air.

The reoxidation of $Re_2Cl_3(dppm)_2(2\text{-mq})$ to $[Re_2Cl_3(dppm)_2(2\text{-mq})]^+$ was accomplished in a controlled and essentially quantitative fashion upon carrying out a bulk electrolysis of the green solution at -0.1 V vs Ag/AgCl. The identity of the cation was confirmed by cyclic voltammetry and ESR spectroscopy.

Preparation of Single Crystals for Structure Determination. Crystals of $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ were grown by the slow diffusion of diethyl ether into dichloromethane solutions of the comlex in a closed system. Suitable dark red crystals were isolated after a period of approximately 3 weeks.

X-ray Crystallography. The structure of $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ was determined by the application of standard procedures. The basic crystallographic parameters are listed in Table I. The cell constants are based on 25 reflections with $18.0 < \theta < 21.0°$. Three standard reflections were measured after every 5000 s of beam time during data collection; there were no systematic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package.

The crystal was found to belong to the monoclinic space group $P2_1/c$ (No. 14). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. With the exception of H(181), the positions for the hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of B(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, they were not included in the least-squares refinement. Hydrogen atom H(181) was located in a difference map and allowed to refine isotropically. An empirical absorption correction was used,[7] the linear absorption coefficient being 46.24 cm^{-1}. No corrections for extinction were applied. The structure was refined by a full-matrix least-squares method where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms of the dirhenium cation and the atoms of the PF_6^- anion were refined anisotropically;

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms of $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ and Their Estimated Standard Deviations[a]

atom	x	y	z	B
Re(1)	0.25880 (2)	0.20437 (1)	0.13125 (1)	2.305 (6)
Re(2)	0.26163 (2)	0.31363 (2)	0.11031 (1)	2.553 (6)
Cl(11)	0.3354 (1)	0.1931 (1)	0.23950 (8)	3.14 (4)
Cl(21)	0.3586 (1)	0.3540 (1)	0.21089 (9)	3.45 (4)
Cl(22)	0.2426 (2)	0.4294 (1)	0.0613 (1)	4.14 (5)
S(12)	0.1655 (2)	0.2926 (1)	0.0045 (1)	3.98 (5)
P(11)	0.1035 (1)	0.2033 (1)	0.1715 (1)	2.80 (4)
P(12)	0.4321 (1)	0.1752 (1)	0.12134 (9)	2.61 (4)
P(21)	0.1182 (2)	0.3489 (1)	0.1561 (1)	3.33 (5)
P(22)	0.4346 (1)	0.3196 (1)	0.09054 (9)	2.57 (4)
N(11)	0.1858 (5)	0.1681 (3)	0.0429 (3)	3.2 (1)
C(12)	0.1512 (6)	0.2092 (5)	−0.0069 (4)	3.7 (2)
C(13)	0.0963 (7)	0.1850(6)	−0.0686 (4)	5.4 (3)
C(14)	0.0840 (8)	0.1194 (6)	−0.0768 (5)	6.3 (3)
C(15)	0.1088 (8)	0.0056 (6)	−0.0341 (6)	7.8 (3)
C(16)	0.1450 (9)	−0.0357 (6)	0.0172 (6)	9.0 (3)
C(17)	0.1960 (8)	−0.0112 (5)	0.0772 (6)	6.9 (3)
C(18)	0.2087 (7)	0.0573 (4)	0.0859 (5)	4.8 (2)
C(19)	0.1217 (7)	0.0744 (5)	−0.0267 (4)	5.4 (2)
C(1A)	0.1723 (6)	0.0996 (4)	0.0338 (4)	3.8 (2)
C(1B)	0.1074 (6)	0.2828 (4)	0.2111 (4)	3.5 (2)
C(2B)	0.5048 (5)	0.2523 (4)	0.1376 (3)	2.7 (2)
H(181)	0.239 (9)	0.091 (6)	0.139 (5)	9 (4)[b]
P(1000)	0.1846 (2)	0.7163 (2)	0.6940 (1)	5.93 (8)
F(1001)	0.0773 (6)	0.7175 (6)	0.7048 (4)	14.0 (3)
F(1002)	0.2323 (8)	0.7132 (7)	0.7644 (5)	18.0 (5)
F(1003)	0.188 (1)	0.7859 (6)	0.699 (1)	28.4 (9)
F(1004)	0.1369 (8)	0.707 (1)	0.6273 (4)	26.2 (7)
F(1005)	0.189 (2)	0.6453 (6)	0.6969 (8)	26.9 (8)
F(1006)	0.2885 (8)	0.7189 (8)	0.6831 (6)	20.6 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$. Data for the phenyl carbon atoms of the dppm ligands are included in the supplementary material. [b] H(181) was refined isotropically.

corrections for anomalous scattering were applied to all atoms so refined.[8] The largest peak in the final difference Fourier map (0.78 e/Å^3) did not appear to be of any chemical significance.

Positional parameters and their errors for the non-phenyl atoms of the compound are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1), a listing of all the positional parameters for the non-hydrogen atoms (Table S2), the positional parameters for the hydrogen atoms (Table S3), the thermal parameters (Table S4), and complete bond distances (Table S5) and bond angles (Table S6) are available as supplementary material.

Physical Measurements. Electrochemical and spectroscopic characterizations were carried out with the use of instrumentation and techniques described previously.[9]

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The transformations observed in this study are summarized in Scheme I. The electrochemical and spectroscopic properties of these complexes have been measured and will by introduced at the appropriate places in the following section. Finally, the single-crystal X-ray structure of $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$ has been determined. The structural data, which have already been mentioned in the Experimental Section, are presented in Tables I–III.

Discussion

Reactions of $Re_2X_4(dppm)_2$ (X = Cl, Br) with 2-Mercaptoquinoline (2-mqH). The ability of a monoanionic bridging ligand

(8) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*; Table 2.2B.
(9) Derringer, D. R.; Fanwick, P. E.; Moran, J.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 1384.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[Re_2Cl_3(dppm)_2(2\text{-mq})]PF_6$[a]

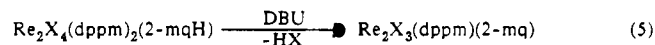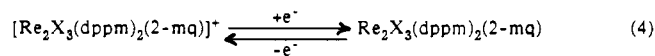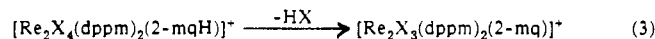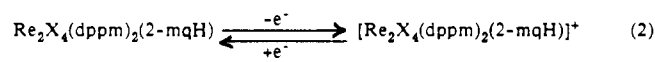|		Distances	
Re(1)–Re(2)	2.2540 (5)	P(21)–C(1B)	1.819 (9)
Re(1)–Cl(11)	2.330 (2)	P(21)–C(2111)	1.818 (9)
Re(1)–P(11)	2.478 (2)	P(21)–C(2121)	1.827 (9)
Re(1)–P(12)	2.489 (2)	P(22)–C(2B)	1.821 (8)
Re(1)–N(11)	2.061 (6)	P(22)–C(2211)	1.818 (8)
Re(1)–H(181)	2.3 (1)	P(22)–C(2221)	1.811 (8)
Re(2)–Cl(21)	2.393 (2)	N(11)–C(12)	1.35 (1)
Re(2)–Cl(22)	2.553 (2)	N(11)–C(1A)	1.40 (1)
Re(2)–S(12)	2.378 (2)	C(12)–C(13)	1.45 (1)
Re(2)–P(21)	2.503 (2)	C(13)–C(14)	1.34 (2)
Re(2)–P(22)	2.496 (2)	C(14)–C(19)	1.41 (2)
S(12)–C(12)	1.71 (1)	C(15)–C(16)	1.38 (2)
P(11)–C(1B)	1.816 (9)	C(15)–C(19)	1.40 (2)
P(11)–C(1111)	1.808 (8)	C(16)–C(17)	1.40 (2)
P(11)–C(1121)	1.816 (8)	C(17)–C(18)	1.40 (1)
P(12)–C(2B)	1.831 (8)	C(18)–C(1A)	1.41 (1)
P(12)–C(1211)	1.819 (8)	C(18)–H(1811)	1.3 (1)
P(12)–C(1221)	1.827 (8)	C(19)–C(1A)	1.42 (1)

		Angles	
Re(2)–Re(1)–Cl(11)	105.85 (6)	Re(1)–Re(2)–Cl(22)	166.97 (6)
Re(2)–Re(1)–P(11)	97.95 (5)	Re(1)–Re(2)–S(12)	89.24 (6)
Re(2)–Re(1)–P(12)	98.65 (5)	Re(1)–Re(2)–P(21)	98.27 (5)
Re(2)–Re(1)–N(11)	100.9 (2)	Re(1)–Re(2)–P(22)	98.40 (5)
Re(2)–Re(1)–H(181)	172 (3)	Cl(21)–Re(2)–Cl(22)	92.51 (8)
Cl(11)–Re(1)–P(11)	81.39 (7)	Cl(21)–Re(2)–S(12)	170.23 (8)
Cl(11)–Re(1)–P(12)	82.48 (7)	Cl(21)–Re(2)–P(21)	81.26 (8)
Cl(11)–Re(1)–N(11)	153.3 (2)	Cl(21)–Re(2)–P(22)	79.16 (7)
Cl(11)–Re(1)–H(181)	82 (3)	Cl(22)–Re(2)–S(12)	77.73 (8)
P(11)–Re(1)–P(12)	159.45 (7)	Cl(22)–Re(2)–P(21)	84.12 (7)
P(11)–Re(1)–N(11)	94.0 (2)	Cl(22)–Re(2)–P(22)	83.45 (7)
P(11)–Re(1)–H(181)	81 (3)	S(12)–Re(2)–P(21)	97.99 (8)
P(12)–Re(1)–N(11)	94.7 (2)	S(12)–Re(2)–P(22)	99.03 (7)
P(12)–Re(1)–H(181)	84 (3)	P(21)–Re(2)–P(22)	156.24 (7)
N(11)–Re(1)–H(181)	71 (3)	Re(1)–H(181)–Cl(18)	118 (8)
Re(1)–Re(2)–Cl(21)	100.51 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme I

$$Re_2X_4(dppm)_2 + 2\text{-mqH} \longrightarrow Re_2X_4(dppm)_2(2\text{-mqH}) \qquad (1)$$

X = Cl or Br

$$Re_2X_4(dppm)_2(2\text{-mqH}) \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Re_2X_4(dppm)_2(2\text{-mqH})]^+ \qquad (2)$$

$$[Re_2X_4(dppm)_2(2\text{-mqH})]^- \overset{-HX}{\longrightarrow} [Re_2X_3(dppm)_2(2\text{-mq})]^+ \qquad (3)$$

$$[Re_2X_3(dppm)_2(2\text{-mq})]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Re_2X_3(dppm)_2(2\text{-mq}) \qquad (4)$$

$$Re_2X_4(dppm)_2(2\text{-mqH}) \overset{DBU}{\underset{-HX}{\longrightarrow}} Re_2X_3(dppm)(2\text{-mq}) \qquad (5)$$
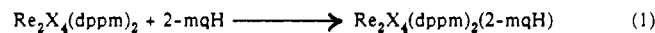
that contains a N–C–S$^-$ unit to complex the dirhenium(II) core has been demonstrated by the reaction of 2-mercaptoquinoline (2-mqH) with $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) in acetone to give the dark purple-black, diamagnetic 1:1 adducts $Re_2X_4(dppm)_2(2\text{-mqH})$. These two complexes show very similar IR spectra (recorded as Nujol mulls) with bands at 1620 s and 1588 s cm^{-1} that are characteristic of the 2-mqH ligand. However, there is an absence of features that could be attributed to the ν(S–H) vibration of a coordinated thiol ligand; this implies that the thiol group is deprotonated and that the ligand is present in its zwitterionic form.[10,11]

A solution of the chloride complex is acetone (1.17×10^{-3} M.) had a conductivity ($\Lambda_m = 57$ Ω^{-1} cm^2 mol^{-1}) that is consistent with a zwitterionic formulation for the 2-mercaptoquinoline ligand in these complexes. A similar situation is encountered in the com-

(10) The IR spectrum of the free ligand 2-mqH as a Nujol mull also shows the absence of a band between 2600 and 2400 cm^{-1} that could be assigned to ν(S–H). This is in line with data for other quinolinethiols.[11]
(11) Hannan, R. B., Jr.; Lieblich, J. H.; Renfrew, A. G. *J. Am. Chem. Soc.* **1949**, *71*, 3733.

plexes $Ru_2(hp)_4Cl\cdot Hhp$[12] and $Rh_2(mhp)_4\cdot Hmhp$,[13] which contain the analogous 2-hydroxypyridine (Hhp) or 2-methyl-6-hydroxy-pyridine (Hmhp) ligands bound through their oxygen atoms, with the unique ionizable hydrogen attached to the nitrogen of the pyridyl ring. The ^1H NMR spectra of the 2-mqH complexes (recorded in CD_2Cl_2) are very similar, with an $ABX_2X'_2$ pattern for the bridgehead $-CH_2-$ protons of the dppm ligands, the most intense components of which are centered at δ +5.56 and δ +5.37 for X = Cl and δ +5.72 and δ +5.50 for X = Br, and an essentially identical and very complex sets of phenyl resonances. A broad resonance at δ +10.16 (X = Cl) and δ +9.80 (X = Br), showing the correct relative intensity, is assigned to the unique proton of the zwitterionic 2-mqH ligand. The corresponding resonance is at δ +12.79 for a solution of 2-mqH in $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectrum of the chloride complex (recorded in CD_2Cl_2) approximates to an $AA'BB'$ pattern, the centers of which are at δ ca. −5.08 and δ ca. −14.14.

An interesting characteristic of these complexes is their electrochemical properties as measured by the cyclic voltammetric technique. Solutions of the complexes in 0.1 M n-Bu_4NPF_6–CH_2Cl_2 show apparently reversible processes at $E_{1/2}$ = +0.08 V and $E_{1/2}$ = +0.83 V vs Ag/AgCl for X = Cl and at $E_{1/2}$ = +0.18 V and $E_{1/2}$ = +0.95 V vs Ag/AgCl for X = Br. Controlled-potential electrolysis experiments showed that each of these processes corresponds to a one-electron oxidation. The cyclic voltammogram of $Re_2Cl_4(dppm)_2\cdot2$-mqH is shown in Figure 1. These characteristics are typical of complexes that contain the triply bonded dirhenium(II) core.[1,5,6,9] The reversibility of the first process (at $E_{1/2}$ = ca. +0.1 V) was demonstrated by carrying out a bulk electrolysis of a solution of the chloride complex at a potential of ca. +0.3 V. Cyclic voltammograms of the resulting solutions were identical with that of the parent 1:1 adduct except that the couple at $E_{1/2}$ = +0.08 V now corresponds to one-electron reduction of the bulk species (n = 1.0 ± 0.1). Also, the oxidized solutions were now ESR-active; an X-band spectrum (recorded at −160 °C) showed a broad, complex signal spanning the range 1.5–4.5 kG and centered at $g \simeq 2.17$ (Figure S1). Electrochemical reduction of these solutions regenerated $Re_2Cl_4(dppm)_2(2$-mqH) and led to loss of this ESR signal. Exactly the same results were obtained when $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in dichloromethane was used as a chemical oxidant to prepare $[Re_2Cl_4(dppm)_2(2$-mqH)]PF_6. Its cyclic voltammetric properties and X-band ESR spectrum were identical with those of solutions of the electrochemically generated cation. Also, a solution of this complex in acetone (1.73×10^{-3} M) had a conductivity (Λ_m = 199 Ω^{-1} cm^2 mol^{-1}) that is greater than that expected for a 1:1 electrolyte;[14] this no doubt reflects the presence of a ionizable proton on the 2-mqH ligand. A similar synthetic procedure was used to prepare $[Re_2Br_4(dppm)_2(2$-mqH)]PF_6, and the identity of this complex was confirmed from its cyclic voltammetric properties.

When dichloromethane solutions of $[Re_2Cl_4(dppm)_2(2$-mqH)]$^+$, that have been generated electrochemically or chemically, are kept at room temperature, they transform into the new chemical species $[Re_2Cl_3(dppm)_2(2$-mq)]$^+$ through the elimination of HCl. This conversion can be monitored conveniently by either cyclic voltammetry or ESR spectroscopy. The cyclic voltammogram of $[Re_2Cl_3(dppm)_2(2$-mq)]$^+$ in 0.1 M TBAH–CH_2Cl_2 shows processes at $E_{1/2}$ = +0.79 V and $E_{1/2}$ = −0.24 V vs Ag/AgCl (Figure 1). The first process corresponds to a one-electron oxidation; the second, to a one-electron reduction. The X-band ESR spectrum of solutions of this cation in CH_2Cl_2 at −160 °C resembles that of $[Re_2Cl_4(dppm)_2(2$-mqH)]$^+$ in showing a broad complex signal centered at $g \simeq 2.17$, but the hyperfine splitting pattern is different (Figure S1).

Pure samples of crystalline $[Re_2X_3(dppm)_2(2$-mq)]PF_6 (X = Cl, Br) can be prepared upon stirring mixtures $Re_2X_4(dppm)_2$-(2-mqH) and $[(\eta^2\text{-}C_5H_5)_2Fe]PF_6$ in dichloromethane or acetone
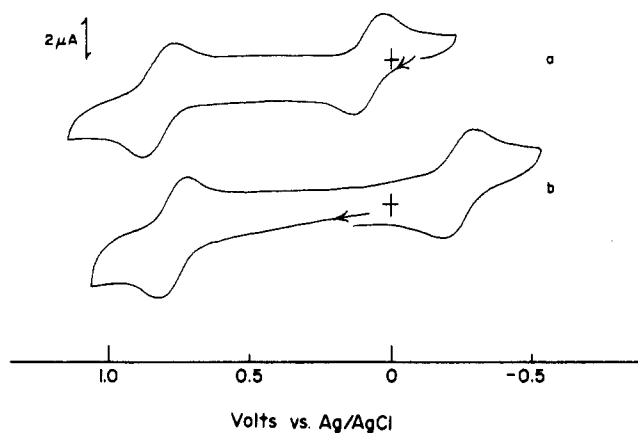
Figure 1. Single-sweep cyclic voltammograms of solutions of (a) $Re_2Cl_4(dppm)_2(2$-mqH) and (b) $[Re_2Cl_3(dppm)_2(2$-mq)]$^+$ in 0.1 M TBAH–CH_2Cl_2 recorded at 200 mV s^{-1} with the use of a Pt-bead electrode. The CV trace in (b) is the same irrespective of whether a solution of the cation is generated through loss of HCl from $[Re_2Cl_4(dppm)_2(2$-mqH)]$^+$ or a sample of $[Re_2Cl_3(dppm)_2(2$-mq)]PF_6 is used.

for several days. The purple products were obtained in yields in excess of 70%. The spectroscopic and electrochemical properties of the chloride derivative are identical with those of the species that is generated in solution by loss of HCl from $[Re_2Cl_4$-(dppm)$_2(2$-mqH)]$^+$. The properties of the bromide are very similar, with $E_{1/2}$(ox) = +0.81 V and $E_{1/2}$(red) = −0.18 V vs Ag/AgCl in the cyclic voltammogram of a solution in 0.1 M TBAH–CH_2Cl_2 and an X-band ESR spectrum (recorded at −160 °C in dichloromethane) that is almost identical with that of the chloride, albeit with slightly less well resolved hyperfine structure (Figure S1). Both complexes dissolve in acetone to give solutions that have conductivities typical of 1:1 electrolytes (Λ_m = 107–117 Ω^{-1} cm^2 mol^{-1} for $c_m \simeq 1.0 \times 10^{-3}$ M).[14] The presence of the PF_6^- anion was confirmed by IR spectroscopy (on Nujol mulls) with the $\nu(P-F)$ mode at 942 cm^{-1}.

The electrochemical reduction of solutions of $[Re_2Cl_3$-(dppm)$_2(2$-mq)]PF_6 in 0.1 M TBAH–CH_2Cl_2 at −0.40 V generates green solutions of the unstable, neutral, diamagnetic complex $Re_2Cl_3(dppm)_2(2$-mq). This same compound can also be prepared by the dehydrochlorination of $Re_2Cl_4(dppm)_2(2$-mqH) upon its treatment with the strong base DBU in dichloromethane solution.

Structural Considerations. Although we have not yet been able to grow suitable single crystals of $Re_2X_4(dppm)_2(2$-mqH) (or the salts of the corresponding monocations) for an X-ray structure determination, it seems reasonable to propose that these complexes have either an A-frame-like structure I, closely akin to that of
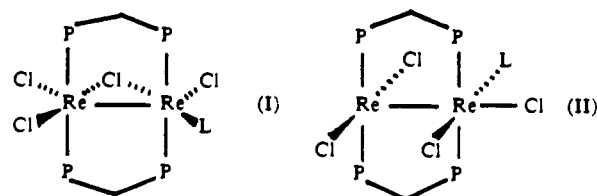

other, structurally characterized, 1:1 adducts of $Re_2X_4(dppm)_2$,[15] or the alternative structure II, in which there are no bridging ligands other than the two μ-dppm bridges. In these structural representations, L is the sulfur-bound 2-mqH ligand, which is most likely present in its zwitterionic form. The major structure change that accompanies dehydrohalogenation of these compounds, as clearly shown by the changes in their electrochemical properties, has been confirmed through a single-crystal X-ray structure determination of $[Re_2Cl_3(dppm)_2(2$-mq)]PF_6. An ORTEP representation of the structure of the dirhenium cation is given in Figure

(12) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.

(13) Berry, M.; Garner, C. D.; Hillier, I. H.; Clegg, W. *Inorg. Chim. Acta* **1980**, *45*, L209.

(14) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(15) Such an example is $Re_2Cl_4(dppm)_2(CO)$: Cotton, F. A.; Dunbar, K. R.; Price, A. C.; Schwotzer, W.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4843.
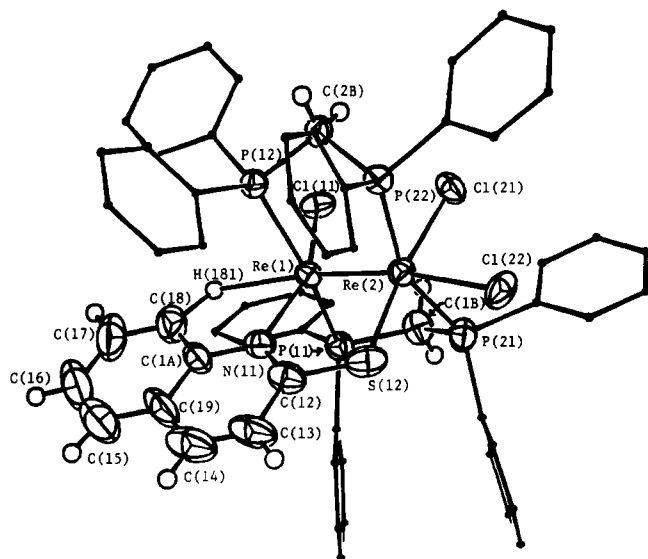
Figure 2. ORTEP view of the structure of the $[Re_2Cl_3(dppm)_2(2\text{-mq})]^+$ cation. For clarity, the atomic numbering scheme is given for all atoms except the phenyl carbon atoms of the dppm ligands and the nitrogen atom of the 2-mq ligand. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius.

2. A trans disposition of bridging dppm ligands is present, and the deprotonated 2-mercaptoquinoline ligand assumes a bridging mode. The Re–Re distance of 2.2540 (5) Å is consistent with a Re–Re bond order of 3.5.[1,5] The structure is slightly twisted away from an eclipsed rotational geometry, although this is hardly surprising in view of the disparate set of ligands. The torsional angles P(11)–Re(1)–Re(2)–P(21), P(12)–Re(1)–Re(2)–P(22), N(11)–Re(1)–Re(2)–Cl(21), and Cl(11)–Re(1)–Re(2)–S(12), which reflect the magnitude of this distortion, are 6.3 (1), 1.5 (1), 4.5 (2), and 5.1 (1)°, respectively. There are three terminal Re–Cl bonds, one of which is collinear with the Re–Re bond and is, as expected, the longest of the three (2.553 (2) Å versus 2.330 (2) and 2.393 (2) Å). Actually, the Re(1)–Re(2)–Cl(22) unit does

deviate somewhat from linearity, with the angle being 166.97 (6)°. While the Re–N and Re–S distances and other parameters associated with the μ-(2-mq) ligand are normal, one feature of special note is that the hydrogen atom (H(181)) on C(18) of the quinoline ring forms a very close contact with Re(1), the Re(1)–H(181) distance being 2.3 (1) Å. While this doubtless reflects, at least in part, the constraints imposed by the rigid planar aromatic ring forcing a close approach of H(181), the associated weakening of the C–H bond (C(18)–H(181) = 1.3 (1) indicates that this may represent an agostic Re···H interaction. In view of the variety and stability of lower valent dirhenium polyhydrides,[16] this is perhaps not unreasonable.

Concluding Remarks. The key features of the chemistry that involves the reactions of $Re_2X_4(dppm)_2$ (X = Cl, Br) with the 2-mqH ligand are summarized by eqs 1–5 in Scheme I. Of particular note is the observation that the oxidation represented by (2) can be accomplished either chemically or electrochemically; this process is of interest, since it is followed by a chemical transformation (3) involving dehydrohalogenation. These complexes represent the first examples of the coordination of a thiolato ligand to a multiply bonded dirhenium unit.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Tables S5), and bond angles (Table S6) and a figure (Figure S1) showing the X-band ESR spectra of $[Re_2Cl_4(dppm)_2(2\text{-mqH})]^+$ and $[Re_2X_3(dppm)_2(2\text{-mq})]PF_6$ (X = Cl, Br) (21 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

(16) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Chapter 43, pp 125–213.

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Formation and Reactions of Bis(trimethylphosphine)–Methyldiborane(4)

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Treatment of $1\text{-CH}_3B_5H_8$ or $2\text{-CH}_3B_5H_8$ with $P(CH_3)_3$ resulted in the cleavage of the pentaborane framework to give $CH_3B_2\text{-}H_3\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$. The methylated diborane(4) adduct $CH_3B_2H_3\cdot 2P(CH_3)_3$ was characterized by mass and NMR spectroscopy, and its reaction chemistry was studied. Hydrogen chloride reacted with $CH_3B_2H_3\cdot 2P(CH_3)_3$ to give $BH_3\cdot P(CH_3)_3$ and $CH_3BHCl\cdot P(CH_3)_3$. The reaction of $CH_3B_2H_3\cdot 2P(CH_3)_3$ with B_4H_{10} in CH_2Cl_2 at -40 °C gave $1\text{-CH}_3B_3H_5\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$. The $1\text{-CH}_3B_3H_5\cdot 2P(CH_3)_3{}^+$ cation isomerized to the $3\text{-CH}_3B_3H_5\cdot 2P(CH_3)_3{}^+$ cation above -35 °C. Likewise, $CH_3B_2H_3\cdot 2P(CH_3)_3$ reacted with B_2H_6 to form $1\text{-CH}_3B_3H_5\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$, which isomerized to $3\text{-CH}_3B_3H_5\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$. Both of these $B_2H_7{}^-$ salts decomposed at room temperature to give $B_3H_7\cdot P(CH_3)_3$, $CH_3B_3H_6\cdot P(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, and $CH_3BH_2\cdot P(CH_3)_3$.

Introduction

An earlier report from this laboratory showed that the treatment of pentaborane(9) with excess trimethylphosphine resulted in the cleavage of the pentaboron framework to give bis(trimethyl-

phosphine)–diborane(4) $[B_2H_4\cdot 2P(CH_3)_3]$ and tris(trimethylphosphine)–triborane(5) $[B_3H_5\cdot 3P(CH_3)_3]$in a 1:1 molar ratio.[1] Subsequently, the reaction chemistry of these cleavage products was investigated, and the results were reported elsewhere.[2-6]

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(1) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.
(2) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.
(3) Snow, S. A.; Shimoi, M.; Ostler, C. D.; Thompson, B. K.; Kodama, G.; Parry, R. W. *Inorg. Chem.* **1984**, *23*, 511. Snow, S. A.; Kodama, G. *Inorg. Chem.* **1982**, *21*, 511.