dimers. Unlike the previously characterized structures, each sulfur ligand is unsymmetrically bridged between the two Mo ions with Mo–S distances of 2.457 (3) and 2.394 (3) Å.

The most notable feature of the iron interaction is its unsymmetrical coordination to the Mo_2S_4 core. Although the Fe–S distances of 2.232 (1) and 2.237 (1) Å are nearly equivalent, Fe_1 is displaced from the plane of the sulfur atoms and tilted toward Mo_{1A}. As a result, the molecule contains a relatively short Fe–Mo distance of 2.853 (3) Å and acute Fe_1–S–Mo_{1A} angles of 76°. The second Mo ion and Fe_1 are bridged by two sulfido ligands in an approximately planar configuration with a much longer metal–metal distance. The short Mo–Fe distance is 0.08–0.15 Å longer than the distances between these metal ions in most of the previously reported sulfido-bridged Mo–Fe clusters.[13-18] However it seems reasonable to assume some bonding interaction between Fe_1Mo_{1A} in I because of the strong tendency of low-spin Fe(II) to be six-coordinate. If this oxidation state formalism is used, the 18-electron Mo(III) ion can be viewed as an electron pair donor to the iron center. This structure provides the first evidence for additional bond formation at the molybdenum ion in the series of tetrasulfido-bridged dimolybdenum complexes.

Different structures have been characterized or proposed when the metal sulfide or the metal carbonyl in eq 1 has been varied. In the reaction of $(MeCp)_2V_2S_4$ with excess iron carbonyl,[5] only one iron was incorporated into the cluster to form $(MeCp)_2V_2S_4Fe(CO)_3$ (II). Sulfur abstraction from II led to the formation of $(MeCp)_2V_2S_3Fe(CO)_3$ which was characterized by an X-ray diffraction study. The trigonal-bipyramidal $M_3(\mu_3\text{-}S)_2$ core involved two equivalent Fe–V distances (2.82 Å) and relatively short $V(\mu\text{-}S)$ distances as a means of alleviating electron deficiency associated with the vanadium ions. The reaction of $[(CH_3)_5C_5MoS_2]_2$ with $Co_2(CO)_8$ has led to the tetrameric product $[(CH_3)_5C_5MoS_2Co(CO)]_2$.[6] The latter complex has been proposed to have a cubane-type structure on the basis of its diamagnetic nature and by analogy to other sulfido-bridged systems. Two clusters with butterfly and planar Mo_2Fe_2 geometries with the formulas $Cp_2Mo_2Fe_2(\mu_3\text{-}S)_2(\mu_{2or3}\text{-}CO)_2(CO)_6$ have been synthesized by the reaction of $Cp_2Mo_2(CO)_4$ with $Fe_2S_2(CO)_6$.[7,8] The cluster reported here is related to the planar isomer by the replacement of two μ-CO ligands with μ_3-sulfido bridges. This results in a formal oxidation of the M_4 system and in the disruption of two of the four Mo–Fe bonds which were present in the carbonyl-bridged cluster.[8]

The reactivity of I is being compared to that of the structurally related Mo dimers with two equivalent organodithiolate bridges. Electrochemical studies suggest that the introduction of additional metal centers into the molybdenum dimers will enable us to develop the chemistry of electron-rich clusters. While complexes of the type $[CpMoSC_nH_{2n}S]_2$ do not show any tendency for electrochemical reduction in the negative potential range up to −2 V vs. SCE, the cyclic voltammetry of I in acetonitrile reveals that it undergoes a reversible reduction at −1.06 V vs. SCE and a second quasi-reversible reduction at −1.45 V. A largely irreversible oxidation is observed near +0.6 V.[19] The dithiometalate bridge of I does not show the lability exhibited by the organodithiolate ligands.[20] For example, no reaction is observed between I and acetylene at 25 °C except in the presence of an oxidizing agent (Me_3NO). Under the latter conditions $[MeCpMoSC_2H_2S]_2$ is formed. The competitive reaction of phenylacetylene and iron carbonyl with $[MeCpMoSSH]_2$ yields primarily the bis(alkenedithiolate) complex, but spectral data[21] suggest that the mixed bridge derivative $(MeCpMo)_2(SCHC(Ph)S)(S_2Fe(CO)_3)$ may also be produced in low yields. Further investigations of the reactivity of both the sulfur ligands and the metal ions in these systems are in progress.

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Registry No. I, 85534-08-3; $[MeCpMo(S)SH]_2$, 75675-65-9; $Fe(CO)_5$, 13463-40-6.

Supplementary Material Available: Tables of interatomic distances and angles, experimental conditions, solution and refinement details, final positional and thermal parameters, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Cyclometalation of (3-Chloropropyl)dicyclohexylphosphine on Rhodium and a Facile, Stoichiometric Rhodium-Assisted Synthesis of the Chelating Triphosphine Ligand $PhP(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)_2$

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Summary: Facile cyclometalation of (3-chloropropyl)dicyclohexylphosphine occurs when $RhCl(COD)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)$ is treated with the secondary–tertiary diphosphine $c\text{-}Hx_2PCH_2CH_2CH_2P(Ph)H$ in the absence of a stronger base. On the other hand, if the same reagents are combined at −78 °C in the presence of NEt_3 and allowed to warm to room temperature over a 2-h period, a clean synthesis of the chelated triphosphine ligand $PhP(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)_2$ results.

Triphosphines that contain trimethylene chains are valuable chelating ligands with the larger transition-metal

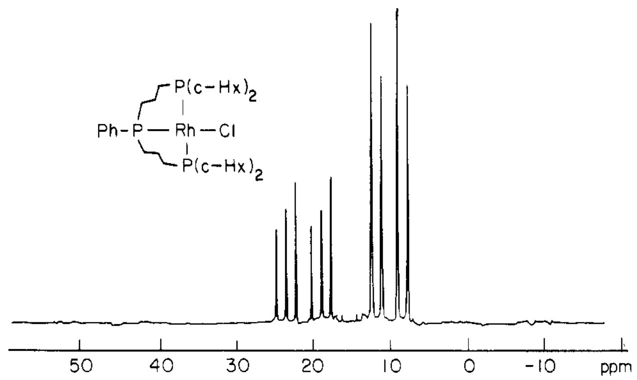

Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of RhCl(Cyttp) in benzene at room temperature.

ions (e.g., Rh, Pt, Ir, Ru).[1] Until recently, the most straightforward route to such ligands involved coupling reactions via Grignard or alkali-metal reagents, and the range of compounds was limited by the stability and availability of the $R_2PCH_2CH_2CH_2Cl$ intermediates.[2] In an effort to develop easier routes to a wide variety of $RP(CH_2CH_2PR'_2)_2$ and $RP(CH_2CH_2CH_2PR'_2)_2$ ligands, we have examined metal-assisted coupling of vinyl, allyl, and (3-chloropropyl)phosphine units to coordinated secondary phosphines.[3] This report describes the successful, high-yield synthesis of $PhP[CH_2CH_2CH_2P(C_6H_{11})_2]_2$ on rhodium and the phospharhodacyclopentane formation with $ClCH_2CH_2CH_2P(C_6H_{11})_2$.

The ligand $PhP(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)_2$, Cyttp, was synthesized in a two-step process by treating $[Rh(\mu\text{-}Cl)(COD)]_2$ with $ClCH_2CH_2CH_2P(C_6H_{11})_2$ (which cleaves the chloride bridges) and then with $(C_6H_{11})_2PCH_2CH_2CH_2P(Ph)H$ (c-HxPPH) (eq 1 and 2). The diphosphine c-HxPPH is added to a solution of I and NEt_3 at −78 °C; as the reaction mixture warms to room temperature, the base (NEt_3) deprotonates the coordinated secondary phosphine. The resultant phosphido group then displaces the chloride from the C–Cl tail of the coordinated $c\text{-}Hx_2PCH_2CH_2CH_2Cl$ ligand and leads to ring closure and RhCl(Cyttp).[4] The $^{31}P\{^1H\}$ NMR spectrum of the resulting complex RhCl(Cyttp), which was isolated in 77% yield, is shown in Figure 1; the chemical shifts and coupling constants of the AB_2X pattern are identical with those of an authentic sample of RhCl(Cyttp), which was prepared by Mazanec and Meek from the tridentate ligand Cyttp and $[Rh(\mu\text{-}Cl)(COD)]_2$.[6] If chelate-ring closure had not occurred, the $^{31}P\{^1H\}$ NMR spectrum of the complex $RhCl(c\text{-}HxPPH)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)$ would have been much more complex than that displayed in Figure 1 because the two $c\text{-}Hx_2P$ groups would be nonequivalent. In addition, the corresponding ^1H and ^{13}C NMR spectra of RhCl(Cyttp) lack the characteristic peaks of the $-CH_2Cl$ group.

$$[Rh(\mu\text{-}Cl)(COD)]_2 + 2c\text{-}Hx_2PCH_2CH_2CH_2Cl \xrightarrow[\text{toluene}]{\text{room temp}} \underset{\text{I}}{2RhCl(COD)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)} \quad (1)$$

$$\text{I} + c\text{-}Hx_2PCH_2CH_2CH_2P(Ph)H \xrightarrow[-78\ °C \rightarrow \text{room temp}]{NEt_3} RhCl(Cyttp) \quad (2)$$

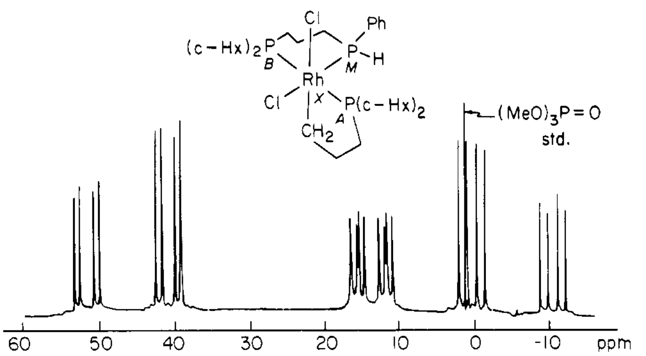

Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of the phospharhodacycle $RhCl(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(c\text{-}HxPPH)$ in dichloromethane at room temperature.

When the steps shown in eq 1 and 2 are performed *without* addition of a base (e.g., NEt_3), a different product is isolated in which oxidative addition of the carbon–chlorine bond to the rhodium atom has occurred. The $^{31}P\{^1H\}$ NMR spectrum of this complex (solvent CH_2Cl_2) is shown in Figure 2. The spectral parameters for the two rhodacyclopentane complexes $RhCl_2(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(c\text{-}HxPPH)$ and $RhCl_2(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(PPH)$, which can be determined from the ABMX spin system (X = ^{103}Rh), are given in Table I.

The P_A nucleus, which belongs to the five-membered phospharhodacyclopentane, is assigned from the low-field chemical shift of that nucleus (47.1 ppm).[7] The second half of the AB pattern consists of the doublet of quartets centered at −4.29 ppm. The large value of $^2J_{P_A\text{-}P_B}$ (406 Hz) indicates that the P_A and P_B nuclei are mutually trans; the trans assignment is supported by the $^1J_{Rh\text{-}P_A}$ and $^1J_{Rh\text{-}P_B}$ values, which are typical phosphorus–rhodium(III) couplings for trans phosphine ligands.[1b,8] Nucleus P_M is assigned to the secondary phosphino group of the c-HxPPH ligand. The P_M multiplet, centered at 14.4 ppm, displays cis-$^2J_{PP}$ couplings to both P_A and P_B. In addition, the ^1H-coupled spectrum shows that $^1J_{P_M\text{-}H}$ is 370 Hz. The relatively large value of $^1J_{Rh\text{-}P_M}$ indicates that P_M is trans to a weak trans influence ligand, i.e., Cl; thus, the structure of $RhCl_2(CH_2CH_2CH_2Ph\text{-}c\text{-}Hx_2)(c\text{-}HxPPH)$ is that shown in Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of $RhCl_2(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(PPH)$, which results analogously from the $Ph_2PCH_2CH_2CH_2P(Ph)H$ ligand (PPH), is almost identical with that of the c-HxPPH complex discussed above. The most significant difference is in the chemical

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(4) In a different study, we have shown by low-temperature $^{31}P\{^1H\}$ NMR that a similar deprotonation of secondary phosphines coordinated to platinum(II) occurs. In the absence of $ClCH_2CH_2CH_2PR_2$ molecules, those platinum phosphide complexes dimerize to give diplatinum phosphido-bridged compounds of the type $[PtZ(c\text{-}HxPP)]_2$ (Z = Cl, CH_3).[5] In the presence of Et_3N and $ClCH_2CH_2CH_2PR_2$ molecules, the platinum reactions also produce chelated triphosphine ligands.[3] [Waid, R. D.; Meek, D. W., manuscript submitted to *Organometallics*.]

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Table I. $^{31}P\{^1H\}$ NMR Spectral Data for the Two Rhodium(III) Metallacycles

	$\delta(P_A)^a$	$\delta(P_B)$	$\delta(P_M)$	$^2J_{P_A-P_B}{}^b$	$^2J_{P_A-P_M}$	$^2J_{P_B-P_M}$	$^1J_{Rh-P_A}{}^b$	$^1J_{Rh-P_B}$	$^1J_{Rh-P_M}$	$^1J_{P_M-H}$
$RhCl_2(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(c\text{-}HxPPH)^c$	47.07	−4.29	14.41	406	27.9	39.0	94.9	86.0	137.5	370
$RhCl_2(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)(PPH)^d$	46.66	0.44	10.94	414	20.7	42.3	101.4	91.5	133.8	360

[a] Chemical shifts are in parts per million from 85% H_3PO_4; chemical shifts that are upfield from the standard are negative. [b] Coupling constants are in hertz. [c] Isolated in 84% yield. Anal. Calcd for $C_{36}H_{62}Cl_2P_3Rh$: C, 56.77; H, 8.21; Cl, 9.30; P, 12.20. Found: C, 55.88; H, 8.41; Cl, 10.00; P, 12.92. [d] Isolated in 85% yield. Anal. Calcd for $C_{36}H_{50}Cl_2P_3Rh$: C, 57.69; H, 6.72; Cl, 9.46; P, 12.40. Found: C, 57.47; H, 6.75; Cl, 9.23; P, 12.56.

shifts of the Ph_2P– and c-Hx_2P– groups of PPH and c-HxPPH, respectively. The $^1J_{Rh-P}$ coupling constants of the PPH and c-HxPPH rhodacycles are consistent with a Rh(III) oxidation state.[6,8]

Steric considerations probably dictate that the two most bulky phosphorus groups are located trans to one another in the resultant rhodacyclopentane. The $^{31}P\{^1H\}$ NMR spectrum of the initial reaction mixture at low temperature is extremely complex; it suggests that several isomeric products are formed initially. However, the spectrum simplifies gradually over several hours until only the final Rh(III) metallacycle appears.

The thermal stability of the carbon–chlorine bond normally restricts oxidative addition reactions to those alkyl chlorides that contain other functional groups which activate the C–Cl bond.[9] Metallacycles have been synthesized previously from substituted arsines and phosphines that contain an alkyl halide; however, in those cases the syntheses have required fairly aggressive reagents. For example, cyclometalation with $Me_2AsCH_2CH_2CH_2X$ or $R_2PCH_2CH_2CH_2X$ (X = Cl, Br) on molybdenum, tungsten, iron, nickel, and rhenium organometallic compounds requires a Grignard reagent (e.g., $R_2PCH_2CH_2CH_2MgX$)[10] or a strong reducing agent (e.g., sodium/mercury amalgam)[11] to produce cycloelimination in phosphine-substituted complexes of the type $(OC)_4BrMPPh_2(CH_2)_nCl$ (M = Mn, Re; n = 1–4). Also, the dianionic maganese complexes $[(OC)_4Mn^{1-}(PR_2O^{1-})]^{2-}$ react with α,ω-bis(triflate)alkanes to give the six-membered heterocycles $(OC)_4MnPR_2OCH_2XCH_2$ (R = Ph; X = CH_2, CMe_2, CH_2CH_2).[12] In contrast to the reactive functional groups noted above, in our reactions the three basic phosphino groups (two c-Hz_2P and one Ph(alkyl)PH) apparently enhance the nucleophilic character of rhodium(I) to the point that facile oxidative addition of the C–Cl bond of a coordinated ω-chloro-1-(diphenylphosphino)alkane occurs.

In contrast to the facile oxidative addition of the C–Cl bond that we observed, Lindner et al.[13] recently found that $[Rh(\mu\text{-}Cl)(CO)_2]_2$ reacts in benzene at 20 °C with similar $ClCH_2CH_2CH_2PR_2$ (R = Ph, Me) molecules with partial CO substitution to give the stable intermediate $RhCl(CO)(R_2PCH_2CH_2CH_2Cl)_2$. Formation of the phospharodacyclopentane required extended periods of heating (e.g., 48 h in refluxing toluene). However, in a reaction reminiscent of the enhanced reactivity of our rhodium(I)–phosphine intermediate, they found that oxidative addition of the C–Cl bond does occur at 20 °C with the more basic complex $Pt(COD)_2$ to form platinacyclopentanes.[13] The implications are (1) that our rhodium(I)–phosphine intermediates $RhCl(c\text{-}HxPPH)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)$ and $RhCl(PPH)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)$ are significantly more nucleophilic than $RhCl(CO)(R_2PCH_2CH_2CH_2Cl)_2$ and (2) that oxidative addition of C–Cl bonds will occur readily

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Organometallics **1983**, *2*, 935–936

in reactions between nucleophilic metals and coordinated (ω-chloroalkyl)phosphines and -arsines.

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Synthesis, Structure, and Fluxional Properties of $Os_3H_3(CO)_9(SiPh_3)$, a Compound with the Formally Unsaturated $Os(\mu\text{-}H)_2Os$ Unit

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Summary: The crystal structure of $Os_3H_3(CO)_9(SiPh_3)$, prepared from $Os_3H_2(CO)_{10}$ and Ph_3SiH, reveals it to contain the formally unsaturated unit $Os(\mu\text{-}H)_2Os$ (Os–Os = 2.7079 (4) Å). The ^{1}H and ^{13}C NMR spectra of the compound indicate the bridging hydrogens and those CO ligands which are bonded to the osmium atoms in the OsH_2Os unit are fluxional.

Our interest[2] in silyl derivatives of osmium clusters has prompted us to investigate the reaction of silanes with the formally unsaturated osmium cluster $Os_3H_2(CO)_{10}$. From the reaction with Ph_3SiH in hexane at 70 °C (in an evacuated sealed flask) the compound $Os_3H_3(CO)_9(SiPh_3)$ (**1**) has been isolated.[3] The crystal structure of this derivative has been solved by conventional X-ray diffraction techniques.[4] The bridging hydrogen ligands were all located although not with great accuracy. As can be seen in Figure 1, the molecule contains doubly hydrogen-bridged, singly hydrogen-bridged, and unbridged osmium–osmium bonds. The osmium–osmium vectors $Os(\mu\text{-}H)_2Os$ = 2.7079 (4) Å, $Os(\mu\text{-}H)Os$ = 3.0103 (4) Å, and Os–Os = 2.8550 (4) Å are entirely consistent with these structural features.[5] The compound is thus similar to the parent compound $Os_3H_2(CO)_{10}$[6] in that it contains the formally unsaturated $Os(\mu\text{-}H)_2Os$ unit. Such groupings are still comparitively rare among transition-metal cluster compounds.[6,7]

The ^{1}H NMR spectrum of **1** in toluene-d_8 solution (Figure 2A) showed three equally intense, high-field resonances, at δ −8.58, −12.29, and −12.42, as expected from the solid-state structure. The ^{1}H NMR resonances for bridging hydride ligands usually occur in the range −15 to −23 ppm.[8] The small upfield shifts (from Me_4Si) observed for **1** can be attributed to the unsaturated nature of the cluster.[8] It is interesting that H(C) which is not directly involved in the OsH_2Os bridge also shows this abnormal shift. The signals at −8.58 and −12.42 ppm exhibited ^{187}Os–^{1}H couplings[9] of 44.1 and 44.9 Hz, respectively, and on the basis of this evidence are assigned to the hydrogen atoms H(A) and H(B) in the double bridge. (We observe a value of 46.9 Hz for this coupling in $Os_3H_2(CO)_{10}$.) For the signal at −12.29 ppm two ^{187}Os–^{1}H couplings were observed: 31.3 and 35.4 Hz.[10] This is interpreted as arising from the coupling of H(C) with the two chemically distinct osmium atoms Os(1) and Os(2) although the evidence is not inconsistent with an asymmetric hydrogen bridge.[11] Another interesting facet of the ^{1}H NMR spectrum of **1** is that the resonances attributable to H(A) and H(B) are sharp singlets (even at −40 °C) and show no evidence of ^{1}H–^{1}H coupling. This suggests there is no mixing of the three center–two electron OsHOs molecular orbitals in the OsH_2Os grouping of **1**.

When a toluene-d_8 solution of **1** is warmed, the ^{1}H NMR signals assigned to H(A) and H(B) broadened indicative of exchange between the two sites. Although the broadening was significant 105 °C (400-MHz operating frequency), the peaks were still far from coalescence. Furthermore, attempts to synthesize **1** specifically labeled with deuterium, by the reaction of $Os_3H_2(CO)_{10}$ with Ph_3SiD, were unsuccessful.[12] (Even in the initial stages the ^{1}H NMR spectrum of the reaction solution showed three equally intense hydride signals due to the product.) This suggested that at the temperature of synthesis (70 °C) there was also exchange between H(C) and the hydrogens in the OsH_2Os unit which was too slow to be detected by NMR line broadening. This was confirmed by spin-saturation-transfer experiments. At room temperature, irradiation of the signal at −8.58 ppm caused marked transfer to the resonance at −12.42 ppm (as expected) but not to that due to H(C) at −12.29 ppm (which, in fact, showed a positive NOE effect) However, at 75 °C there was significant transfer to the signal at −12.29 ppm as illustrated in Figure 2B.

The ^{13}C NMR spectrum (natural abundance) of **1** in CD_2Cl_2 at room temperature showed nine resonances (180.1, 178.3, 177.3, 175.9, 173.8, 172.2, 172.1, 166.8, 166.6 ppm) which is, again, what one would expect from the solid-state structure. However, in toluene-d_8 at 100 °C (^{13}C-enriched sample) the four signals at 174.0, 172.1, 166.6, and 166.4 ppm remained sharp but the others had almost completely collapsed into the base line. These results are

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(3) The reaction period was 7 h, and the compound was separated (58% yield) from $Os_3H_2(CO)_{10}$ and **2** by chromatography on silica gel with hexane–benzene as the eluant. Data for **1**: yellow-orange crystals; mp 150–152 °C; IR (hexane) ν(CO) 2129 (m), 2079 (s), 2054 (s), 2048 (s), 2038 (s), 2025 (m), 2007 (ms), 1974 (m) cm^{-1}; MS m/e 1086 $(P)^+$. Anal. Calcd for $C_{27}H_{18}O_9SiOs_3$: C, 29.89; H, 1.67. Found: C, 29.75; H, 1.55.

(4) Crystal data (at 20.8 °C): space group $P2_1/c$; a = 19.837 (2) Å, b = 9.983 (1) Å, c = 15.385 (1) Å, β = 98.62 (1)°, V = 3012.3 Å^3, Z = 4, ρ_{calcd} = 2.392 g cm^{-3}. Intensity data were collected by line profile analysis on a Picker FACS-I automated diffractometer, graphite-monochromated Mo Kα radiation, to give 3951 reflections $I > 2.3\sigma(I)$. The structure was solved by heavy-atom methods. Non-hydrogen atoms were refined with anisotropic temperature factors. The bridging hydride atoms were refined in the least squares (fixed U), but the phenyl hydrogen atoms were held at calculated positions. Final R_F = 0.021 and R_{wF} = 0.025. Bond lengths quoted in Figure 1 are without thermal motion corrections.

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(10) We have measured the ^{187}Os–^{1}H couplings of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$[2] as 32.3 and 36.8 Hz (CD_2Cl_2 solution). Note also that Lewis and coworkers found ^{187}Os–^{1}H couplings in the range 14.4–38.1 Hz for bridging hydride ligands in saturated osmium clusters.[9]

(11) The OsHOs bridges as determined by the diffraction study are all asymmetric. Because of the large errors associated with the hydrogen coordinates, it cannot be certain that these asymmetries are genuine, although it would not be unreasonable in view of the different chemical characters of the three osmium atoms.

(12) Contact with chromatographic material, which is known to cause hydrogen–deuterium exchange in $Os_3H_2(CO)_{10}$[13] was avoided in these experiments.

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