First and foremost, it is observed that the positively charged sulfur atom is formally coordinated to the molybdenum atom. Second, the approximately octahedral coordinating geometry about the metal atom is confirmed. The molecular structure of II is very similar to that of I; however, its metal–sulfur bond distance at 2.547 (1) Å is 0.135 Å longer than that in I, 2.412 Å. The molybdenum–carbon distance to the carbonyl ligand trans to the molybdenum–sulfur bond at 1.944 Å is slightly shorter than the corresponding distance of 1.957 (4) Å observed in II. The shortness of the metal–sulfur bond in I implies that it is stronger than that in II, but this does not produce an observable weakening of the bond trans to it as would be expected on the basis of the π back-bonding theory.[11,12] However, structural trans effects are not usually large and in some cases have not been observed when expected.[13] In addition, it has been proposed that trans effects are also influenced by σ bonding,[14] and a ligand with a weak σ inductive effect would lead to a strengthening of the bond trans to it. If sufficiently weak, this might completely offset the weakening effect caused by the π back-bonding. Bond distances to the ligands cis to the Mo–S bonds are similar in both I and II. Thus, there is also no observable structural cis effect.

Infrared spectra show that the absorption frequencies of the carbonyl ligands in I are significantly higher than those in II.[15] This further supports the notion that the coordinated sulfonium group in I is strongly withdrawing electron density from the metal atom. π back-bonding would seem to be the most likely mechanism.

The shortness of the molybdenum–sulfur bond in I suggests that it is thermodynamically quite stable; however, reactivity studies show that in reactions with nucleophiles, it is kinetically labile. For example, under an atmosphere of carbon monoxide, I reacts over a period of 8 h. in CH_2Cl_2 solvent to form $Mo(CO)_5[PPh_2(CH_2)_2SMe_2]^+BF_4^-$.[16] Over the same period of time, II shows no significant reaction with CO. Parry showed that the cationic complex $Fe(CO)_4[PNMe(CH_2)_2NMe]^+$ was also unusually reactive in nucleophilic substitution reactions, but for this complex it was the ancillary carbonyl ligands and not the positively charged ligand which was replaced.[4b]

In summary, it has been found that the coordinate bond between a metal atom and sulfonium cation is unusually short. Interestingly, this ligand does not produce a significant structural trans-weakening effect. Further studies of the structure, bonding and reactivity of this unusual coordinate bond are in progress.

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Supplementary Material Available: Complete tables of structure factor amplitudes, fractional atomic coordinates, bond distances, and bond angles are available for both crystal structures (39 pages). Ordering information is given on any current masthead page.

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(15) IR (CH_2Cl_2): for I ν(CO) 2048 (s), 1965 (m, sh), 1943 (vs, br) cm^{-1}; for II ν(CO) 2023 (ms), 1913 (s), 1869 (ms) cm^{-1}.

(16) For $Mo(CO)_5[PPh_2(CH_2)_2SMe_2]^+BF_4^-$; IR ($CH_2Cl_2$) ν(CO) 2075 (ms), 1996 (w), 1946 (vs, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (m, Ph), 3.19 (br, CH_2), 2.93 (s, Me), 2.87 (br, CH_2); yield 88%.

Homogeneous Activation of the C–H Bond. Formation of Phenylsiloxanes from Benzene and Silicon Hydrides

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Summary: Pentamethyldisiloxane reacts with benzene under catalysis by Vaska's compound to yield phenylsiloxanes and other redistribution products. The compound $Ir(Ph)(CO)L_2$ (L = Ph_3P) reacts with pentamethyldisiloxane in a very unusual fashion to give a series of methylsiloxane oligomers end-capped with one or two phenyl groups.

Homogeneous activation of the C–H bond to substitution of hydrogen by other functionalities is one important goal of current chemical research. There are now a goodly number of reports which describe the reactions of metal complexes with C–H bonds to give insertion products of the type M(H)R or M(H)Ar (R = alkyl, Ar = aryl).[1] However, we know of only one report which describes a catalytic activation–substitution, other than simple H/D exchange, on a C–H bond. That is the brief description by Parshall of the reaction of benzene with triethylaluminum in the presence of Cp_2NbH_3 to yield phenyldiethylaluminum.[2,3] We wish to report the second such activation–substitution of an aromatic C–H bond: the reaction of benzene with silyl hydrides in the presence of iridium(I) complexes to give phenylsilanes.

The activity of some group 8 metal complexes, including those of Ir, Rh, Pt, and Pd, for the catalyzed oligomerization of tetraalkyldisiloxanes (eq 1) has been described.[4]

$$(n+1)(HMe_2Si)_2O \xrightarrow{[cat.]} nMe_2SiH_2 + \underset{E'D_nE'}{HMe_2Si(OSiMe_2)_nOSiMe_2H} \quad (1)$$

In effect, the oligomerization reaction represents a catalyzed exchange of SiO groups for H in the Si–H bond (referred to as an SiO/H exchange). Further investigation[5–7] has revealed that slower Me/H and SiO/Me exchanges also occur in these systems, resulting in complex mixtures. For example, when pentamethyldisiloxane, $Me_3SiOSiMe_2H$, was stirred in benzene with 2 mol % of Vaska's complex $L_2(CO)IrCl$ under N_2 at 60 °C, the

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(1) The following list of leading references is representative: (a) Parshall, G. W. *Catalysis (London)* **1977**, *1*, 335. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 123–128. (c) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (d) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950. (e) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (f) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188. (g) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (h) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *Ibid.* **1977**, *99*, 7870.

(2) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

(3) Metal ions which are strong Lewis acids, e.g., Pd^{2+} will, in the presence of oxygen, catalyze the coupling of arenes to biaryls etc.[1a,b,f] The mechanisms of these reactions are not well documented, but probably σ-arylmetal complexes are formed via Friedel–Crafts type reactions (see ref 1b,f). These electrophilic substitutions are considered outside the scope of the "insertion" type discussed here.

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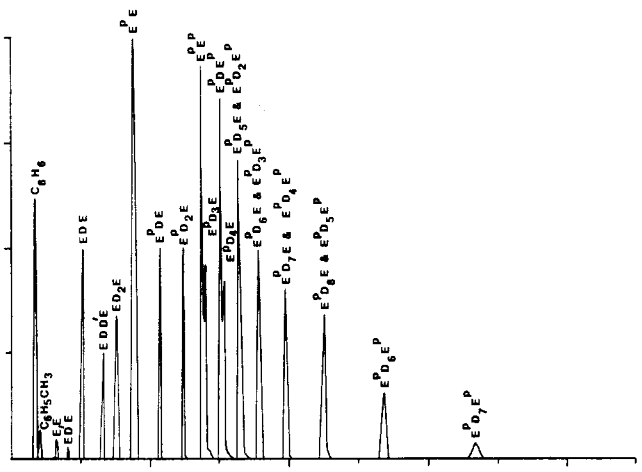

Figure 1. Total ion trace of the GC–mass spectrm of the mixture from the reaction of pentamethyldixiloxane and $L_2(CO)IrPh$ (1) (1:1). The notation here and in the text is as follows: E = $Me_3SiO_{1/2}$; D = $Me_2SiO_{2/2}$; D′ = $MeHSiO_{2/2}$; E^P = $Me_2PhSiO_{1/2}$; E′ = $HMe_2SiO_{1/2}$. Thus, $PhMe_2SiOSiMe_2OSiMe_3$ is written as E^PDE.

products include $Me_3SiOSi(H)MeOSiMe_3$ (ED′E, 75%), $Me_3SiOSiMe_2OSiMe_3$ (EDE, 5%), and $Me_3Si(OSiMe_2)_2OSiMe_3$ (ED_2E, 4%) (the shorthand notation, ED_nE etc., is explained in the caption to Figure 1). Also detected in this mixture was the phenylsiloxane, $PhMe_2SiOSiMe_3$ (E^PE, 2%). Similarly, small (1–2%) yields of phenyltetramethyldisiloxane, $PhMe_2SiOSiMe_2H$ (E^PE'), were detected when tetramethyldisiloxane was treated with $L_2(CO)IrCl$ or L_3RhCl (L = Ph_3P) in benzene.

The source of the phenyl groups was easily established by running the redistribution reactions in benzene-d_6. When $L_2(CO)IrCl$ was the catalyst precursor the resulting phenylsiloxanes were d_5 substituted. No deuterium was incorporated into the phenyl groups of the phenylsiloxanes when L_3RhCl was the catalyst precursor, thus, indicating that in this case the phenyl groups are coming from the Ph_3P ligands of the rhodium complex.[8]

Since it could be argued that the low yields of phenylsiloxanes did not demonstrate true catalysis, we sealed a mixture consisting of 20 mL of benzene, 35.9 mmol of pentamethyldisiloxane, and 0.746 mmol of $L_2(CO)IrCl$ in an ampule and heated this mixture to 100 °C for 49 days. At the end of this time, the ampule was opened, and the contents were subjected to a GC/MS analysis. The mixture consisted of the expected redistribution products and phenyl siloxanes, the major components being Me_3SiH (9%), EE′ (22%), E′DE′ (13%), EDE (7%), $E'D_2E'$ (5′), ED_2E (10%), E^PE (17%), E^PE^P (2.5%), and about 2% total of the phenylsiloxanes E^PDE', E^PDE, E^PDE^P, E^PD_2E', and E^PD_2E. The product mix corresponds to a total of 10.0 mmol of Si–Ph bonds or 13.4 Si–Ph bonds formed per Ir.

A possible catalysis cycle for the formation off Ph–Si bonds is shown in eq 2–4. The net reaction is shown in eq 5 (M = $L_2(CO)Ir$, R = e.g., Me_3SiO).

$$\mathrm{M{-}Cl + RMe_2SiH \rightleftarrows [M(H)(Cl)SiMe_2R] \rightarrow M{-}H + RMe_2SiCl} \quad (2)$$

$$\mathrm{M{-}H + Ph{-}H \rightleftarrows [MH_2Ph] \rightleftarrows M{-}Ph + H_2} \quad (3)$$

$$\mathrm{M{-}Ph + RMe_2SiH \rightleftarrows \underset{1}{[M(H)(Ph)(SiMe_2R)]} \rightleftarrows MH + PhSiMe_2R} \quad (4)$$

$$\mathrm{PhH + RMe_2SiH \rightarrow H_2 + RMe_2SiPh} \quad (5)$$

The first step (eq 2), i.e., the formation of silyl chlorides and metal hydrides, has been observed previously.[4,9,10] In order to test the feasibility of eq 4, we prepared the phenyliridium complex, $L_2(CO)IrPh$,[11] and allowed it to react with pentamethyldisiloxane (E′E) (1:1) at 60 °C in benzene for 1 h. Rather surprisingly, the *simple* oxidative addition–reductive elimination reaction (eq 4) does not occur. Instead, a remarkable series of oligomers, E^PD_nE and $E^PD_nE^P$, end-capped with one or two phenyls is produced in addition to some of the products which arise from the catalyzed redistribution of groups on the starting disiloxane (see Figure 1).

The course of this remarkable reaction is at present unclear. Presumably, under the influence of $L_2(CO)IrPh$ or one of its reaction products, some pentamethyldisiloxane (EE′) disproportionates into tetramethyldisiloxane (E′E′) and hexamethyldisiloxane. The EE′ and E′E′ are then oligomerized into $E'D_nE$ and $E'D_nE'$ which in turn react via H/Ph exchange to give the observed products, E^PD_nE and $E^PD_nE^P$, respectively.[12]

When this stoichiometric reaction of $L_2(CO)IrPh$ and pentamethyldisiloxane was carried out in C_6D_6 solvent, two things were apparent. First, benzene (C_6H_6) was detected, suggesting that intermediates, e.g., 1 can reductively eliminate any of the three possible products, C_6H_6, RMe_2SiH, or RMe_2SiPh. Second, very little (<2%) C_6D_6-derived phenyl was incorporated into the initially formed phenylsiloxanes. However, on standing for 7 days at room temperature, the mixture becomes more complex due to further redistribution reactions on silicon, and the phenylpentamethyldisiloxane (E^PE) became enriched to 40% C_6D_5 groups. This enrichment is *not* due to H/D exchange since no intermediate stages of deuterium incorporation, $C_6H_{5-n}D_n$, were found. Thus, the rate of benzene activation is less than the rate of siloxane disproportionation. The rate of siloxane disproportionation is comparable to, or faster than, the rate of Ph/H exchange on silicon as expressed in eq 4.

At this point, we wish to stress two things. First, the potential for the catalytic formation of phenylsilanes from benzene and silyl hydrides has been demonstrated. A route to these compounds which does not involve chlorinated aromatics may have technological implications. Second, the catalyst system used here is by no means optimized for CH activation. Surely, nonproductive insertion into the ortho CH bonds of the Ph_3P ligands competes with insertion into the benzene C–H bonds (see especially ref 1c). We are presently testing more suitable complexes for the catalysis of reaction 5.

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Registry No. pentamethyldisiloxane, 1438-82-0; benzene, 71-43-2; $(Ph_3P)_2(CO)IrPh$, 42402-07-3; $(Ph_3P)_2(CO)IrCl$, 15318-31-7; $Me_3SiOSi(H)MeOSiMe_3$, 1873-88-7; $Me_3SiOSiMe_2OSiMe_3$, 107-51-7; $Me_3Si(OSiMe_2)_2OSiMe_3$, 141-62-8; Me_3SiH, 993-07-7; $HMe_2Si(OSiMe_2)_2OSiHMe_2$, 1000-05-1; $PhMe_2SiOSiMe_3$, 14920-92-4; $PhMe_2SiOSiMe_2Ph$, 56-33-7.

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(8) A reviewer raised the possibility that the phenyl-containing products might be artificats of the analysis method. This possibility is rejected for the following reasons (1) the same GC curves were obtained on two separate instruments, (2) the extent of phenyl incorporation is independent of whether or not solvent was removed before GC analysis, and (3) the product mix and extent of phenyl incorporation changes with time, which would not be the case if the products were forming in the mass spectrometer or the GC column. No differences were observed between product analyses conducted by transferring all volatiles from the metal complexes by trap to trap vacuum transfer followed by GC analysis or by simply injecting the reaction mixture onto the GC column.

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(12) The iridium-containing product, an off-white solid, appears to be a mixture of hydrides $L_2(CO)IrH_3$ and $L_2(CO)IrH$ and hydrides arising from insertion into the ortho C–H bonds of the ligands.