increased amounts of diamagnetic III.

On cooling the latter solution from 95 to 35 °C, the broad ($\Delta\nu_{1/2} \approx 180$ Hz), averaged methyl resonance shifts downfield from $\delta \sim 29.0$ to $\delta \sim 32$; the correlation of chemical shift with temperature appears to be consistent with Curie law behavior.[12] Interestingly, however, on further cooling, the apparent Curie law behavior is lost, as the methyl resonance reverses the trend and shifts upfield, presumably because of an increasing contribution of the methyl resonance of the diamagnetic III to the averaged chemical shift. The spectrum remains invariant below −75 °C, a sharp singlet at δ 1.54 being attributable to III.

Solutions of III/IV exhibit pronounced chemical reactivity characteristic of metal-centered radicals, as shown in Scheme I. While benzene solutions seem indefinitely stable at room temperature under rigorous exclusion of air and light, conversion to $[(\eta^5\text{-}C_5Me_5)Cr(CO)_2]_2$[4b] occurs on protracted heating above 40 °C or on exposure to sunlight. As with the $\eta^5\text{-}C_5H_5$ analogue,[1d,2] IV is very substitution-labile and readily reacts with ^{13}CO to give ^{13}CO-enriched material, as shown by changes in the IR spectrum. Similarly, reactions with *t*-BuNC and smaller tertiary phosphines (PMe_3, PMe_2Ph, $P(OMe)_3$, but not the larger PPh_3) result in the formation of extremely air-sensitive, monosubstituted compounds of the type $[(\eta^5\text{-}C_5Me_5)Cr(CO)_2L]$. The substituted compounds are thermally labile and have not been successfully purified. However, they have been identified by their IR spectra (Table I), which are very similar to those of compounds of the type $[(\eta^5\text{-}C_5H_5)Cr(CO)_2L]$,[2] by their paramagnetism (one unpaired electron), by the presence of very broad resonances in the ^1H NMR spectra, and by the mass spectra of the PMe_3 and PMe_2Ph derivatives, which exhibit peaks at m/z values corresponding to the M^+, $(M - CO)^+$, and $(M - 2CO)^+$ ions. The steric restrictions to substitution reactions of IV are evident from the lack of reaction of PPh_3; both this ligand and tricyclohexylphosphine form derivatives in the $\eta^5\text{-}C_5H_5$ system.[2]

Solutions of III/IV also take part in atom abstraction reactions typical of other 17-electron compounds,[3] reacting with bromine and iodine to form the known halo compounds $(\eta^5\text{-}C_5Me_5)Cr(CO)_3X$ (X = Br, I)[13] and with carbon tetrachloride to form the chloro analogue (Scheme I). As has been reported,[13] the bromo and iodo compounds are very labile and cannot be purified satisfactorily; the chloro compound is similarly difficult to work with. However, all three compounds were readily identified on the basis of comparisons of their spectroscopic properties, as shown in Table I. Interestingly, $(\eta^5\text{-}C_5Me_5)Cr(CO)_3I$ takes part in an iodine atom exchange process with IV, as evidenced by coalescence of the methyl resonances of the two compounds. This type of exchange does not occur for the compounds $(\eta^5\text{-}C_5Me_5)Cr(CO)_3X$ (X = H, Cl, Br), although it is a common feature of the chemistry of II.[2]

Compound IV also takes part in atom abstraction processes, reacting with methyl iodide, benzyl bromide, allyl bromide, and tri-*n*-butyltin hydride, as shown in Scheme I. In all cases, the products have been difficult to separate and/or have proven to be too labile to purify, and all have been of necessity identified spectroscopically. Thus the halo products were characterized on the basis of the spectroscopic data discussed above and presented in Table I, while the methyl,[14] benzyl, and allyl compounds were characterized by their IR and NMR properties (Table I) (and by the similarities of these properties to those of analogous $\eta^5\text{-}C_5H_5$ compounds[2]) following synthesis by other routes, such as reaction of the anion $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]^-$[13] with the appropriate organic halide or of $(\eta^5\text{-}C_5Me_5)Cr(CO)_3I$ with alkyllithium reagents.

Interestingly, while the primary alkyl compound 2-phenethyl bromide does not react with IV, the benzylic isomer 1-phenethyl bromide does, albeit in a different fashion than anticipated. As shown in Scheme I, the products are $(\eta^5\text{-}C_5Me_5)Cr(CO)_3Br$, $(\eta^5\text{-}C_5Me_5)Cr(CO)_3H$, and styrene. Evidently bromine abstraction does occur, but the thus formed secondary alkyl radical undergoes hydrogen abstraction by a second molecule of IV.

The hydride product of the reaction of IV with $n\text{-}Bu_3SnH$ was characterized by its spectroscopic properties (Table I), the oily tin-containing compound by comparison of its spectroscopic properties with those of a sample made by treating $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]^-$[13] with $n\text{-}Bu_3SnCl$.

Acknowledgment. We are indebted to the National Science and Engineering Research Council for financial support.

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Kinetics and Mechanism of the Pyrolysis of 1,1-Dimethylsilacyclopent-3-ene

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Summary: Experimental kinetic data for the pyrolysis of the title compound and the formation of it and an isomer by addition of dimethylsilylene to butadiene are reported and shown to be consistent with a nonconcerted mechanism involving vinylsilacyclopropane intermediates. The mechanism closely approximates to steady-state conditions, with no single rate-determining step.

When we used buta-1,3-diene as a trap for dimethylsilylene during our studies of the silene $\rightleftharpoons$ silylene isomerization, $HMeSi{=}CH_2 \rightleftharpoons {:}SiMe_2$, we noted that silylene addition to form the principal adduct 1,1-dimethylsilacyclopent-3-ene (1) was reversible.[1] Lei and Gaspar[2] subsequently investigated the vacuum flow pyrolysis of 1 at 700 °C, confirming that extrusion of dimethylsilylene was the major reaction, accompanied by some isomerization of 1 to 1,1-dimethylsilacyclopent-2-ene (2). Very reasonably, they suggested that pyrolysis of 1 and the reverse addition of dimethylsilylene to butadiene might follow nonconcerted mechanisms involving a vinylsilacyclopropane intermediate; they have obtained good evidence for such mechanisms from the product composition of the pyrolysis of 1,1,2-trimethylsilacyclopent-3-ene[2] and from the addition of dimethylsilylene to methyl-substituted butadienes.[3]

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Table I. Pyrolysis of 1,1-Dimethylsilacyclopent-3-ene Arrhenius Parameters for Formation of Products

product	log A/s^{-1}	$E/\mathrm{kJ \cdot mol^{-1}}$
2	12.3 ± 0.6	251 ± 9
3	11.9 ± 0.2	230 ± 4

Scheme I

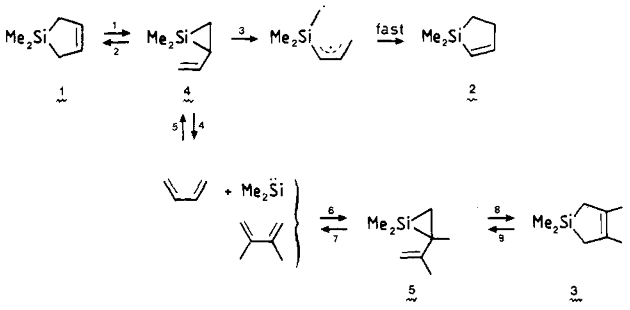

Table II. Estimated Arrhenius Parameters for Reactions in Scheme I

reactn	log A/s^{-1}	$E/\mathrm{kJ \cdot mol^{-1}}$	source
1	12.2	232	*a*
2	12.5	108	*a*
3	13.5	135	*a*
4	13.0	111	*a*
5	10.7	0	*b*
6	10.7	0	*a*
7	13.0	111	*a*
8	12.5	108	*a*
9	12.2	232	*a*
product	**log A/s^{-1}**	**$E/\mathrm{kJ \cdot mol^{-1}}$**	**source**
2	12.2	252	*c*
3	11.9	230	*c*

[a] See text. [b] Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 515. [c] Computed Arrhenius parameters for formation of products.

Although the system comprising pyrolysis of 1 and the reverse addition of dimethylsilylene to butadiene has the drawback of lacking stereochemical markers, it has the advantage of being the simplest system of this type, with a minimal number of products. It is therefore the most suitable starting point for our efforts to contribute to understanding of these intriguing and topical reaction mechanisms through gas kinetics experiments. Compound 1 was pyrolyzed in our stirred-flow apparatus (SFR)[4] between 609 and 663 °C with a 10-fold excess of 2,3-dimethylbuta-1,3-diene; we established from separate experiments[5] that addition of dimethylsilylene to 2,3-dimethylbuta-1,3-diene gave only one adduct, 1,1,3,4-tetramethylsilacyclopent-3-ene (**3**). Products were identified by GC/mass spectrometry (HP5995C), while kinetic measurements were based on GC peak areas. First-order rate constants for the formation of **2** and **3** are in Table I.[6] These were the two main products of interest, but 1,1-dimethylsilacyclopentadiene was also a significant product, and there were several others;[7] lacking calibration data for all of these, we were unable to calculate a material balance, but we do not believe that there was substantial loss of material from the gas phase. Complementary kinetic evidence to that in Table I comes from our recent work[8] on the reverse process, the addition of dimethylsilylene to butadiene to form **1** and **2**; we found that the relative yields of **1** and **2** decreased from 9.5:1 at 436 °C to 7.7:1 at 470 °C; i.e., the activation energy for the formation of **2** is 27 kJ·mol^{-1} higher than that for the formation of **1**.

A reasonable mechanism combining the foregoing processes through vinylsilacyclopropane intermediates[2,3] is in Scheme I. For reasons explained elsewhere,[8] we believe reactions 2 and 8 to be direct 1,3-silyl shifts, and have therefore assumed that reactions 1 and 9 are as well. The mechanism may be tested by numerical integration,[1] but that is complicated by the shortage of kinetic and thermochemical data for these compounds. The most suitable starting point appears to be the comparison between reaction 3 and its hydrocarbon counterpart. The Arrhenius parameters for the isomerization of vinylcyclopropane to cyclopentene[9] are log $A/s^{-1} = 13.5$ and $E/\mathrm{kJ \cdot mol^{-1}} = 208$, implying the development of full allylic stabilization in the transition state. Reaction 3 should have a similar *A* factor, but a lower activation energy because of the high ring strain in **4**. The ring strain in silacyclopropane has recently been calculated[10] to be 181 kJ·mol^{-1}, i.e., 73 kJ·mol^{-1} higher than in cyclopropane; if the same differential applies to the vinyl-substituted systems, $E_3 = 135$ kJ·mol^{-1}. We then used $(E_3 - E_4) \simeq 21$ kJ·mol^{-1} (from Table I) and $(E_3 - E_2) \simeq 27$ kJ·mol^{-1} (from ref 8, vide supra) to obtain initial estimates of E_2 and E_4. We assumed that $k_6 = k_5$, $k_7 = k_4$, $k_8 = k_2$, and $k_9 = k_1$. It seemed likely that formation of either **2** or **3** would be approximately rate-determined by reaction 1; Arrhenius parameters for reaction 1 based on those for formation of **2** were irreconcilable with the experimental results, but Arrhenius parameters for reaction 1 similar to those for formation of **3** were much more satisfactory. It was possible to estimate reasonable *A* factors and to make minor adjustments to the assumed activation energies so as to produce excellent agreement with the experimental results, both for pyrolysis of **1** and for addition of dimethylsilylene to butadiene,[8] simulated by reactions 1–5 in Scheme I plus a reaction forming dimethylsilylene from a disilane precursor. The resulting Arrhenius parameters are in Table II, which also contains the computed Arrhenius parameters corresponding to the experimental results in Table I. The calculated Arrhenius parameters for reaction 2 look reasonable in relation to those for the 1,3-trimethylsilyl shift in an acyclic allyl system,[11] having about the same *A* factor and a lower activation energy because of ring strain. The *A* factor for dimethylsilylene extrusion (reaction 4) is also reasonable for a concerted process; the low activation energy implies considerable stabilization energy in dimethylsilylene.[12]

These calculations not only confirm that the reactions in Scheme I constitute an entirely reasonable mechanism but also provide some new insight into it. Formation of **2** is not rate-determined by reaction 1, while formation of **3** only approximates to being so. The computed concentrations of the vinylsilacyclopropane intermediates **4** and **5** are about as low as that of dimethylsilylene; i.e., all of these intermediates are closer to being in a steady state. Indeed, a simple steady-state calculation neglecting reac-

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tions 5 and 9 (the computations show the former to be ca. 100 times slower than reaction 6) gives $d[2]/dt \simeq k_1k_3[1]/(k_2 + k_3 + k_4)$ and $d[3]/dt \simeq k_1k_4[1]/(k_2 + k_3 + k_4)$. Over the temperature range in question, $k_3/(k_2 + k_3 + k_4)$ has a temperature dependence of ca. 23 kJ·mol^{-1}, while the temperature dependence of $k_4/(k_2 + k_3 + k_4)$ is ca. −1 kJ·mol^{-1}, both agreeing quite well with the results of the more accurate numerical integration calculation.

Thus, there is no single rate-determining step in Scheme I; of course, the *rate constant* k_1 is much less than the others, but the *rates* of individual reactions are closer to each other because the concentrations of the intermediates are so small.

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Solid-State Organometallic Chemistry of Molecular Metal Oxide Clusters: C–H Activation by an Iridium Polyoxometalate

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Summary: Hydrogenation of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ in a solid–gas reaction produces $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$. EXAFS studies of the molybdenum analogue indicate the presence of isolated, lattice-stabilized $(Ph_3P)_2IrH_2^+$ ions. H—D exchange with $CD_3CH{=}CH_2$ occurs via a reversible C—H addition reaction that also produces $[(Ph_3P)_2IrH(\pi\text{-}C_3H_5)]_3PW_{12}O_{40}$ and scrambles the $C_3D_3H_3$ deuterium label. Exchange with toluene is selective and involves activation of aromatic but not aliphatic C–H bonds. Slow exchange with c-C_6D_{12} also occurs.

We are investigating the solid-state chemistry of materials formed from organometallic cations and anionic molecule metal oxide clusters[1,2] and have synthesized iridium oxometalates which, in their heterogeneous reactions with small organic molecules, exhibit substantial scope and diversity, here illustrated by C–H activation processes. It will be seen that incorporation of such cations into polyoxometalate lattices drastically changes the course of both preparative and reaction chemistry which are qualitatively and unexpectedly different from that observed in related homogeneous systems.

Table I. Distribution of Deuterium in $[(Ph_3P)_2Ir(H,D)(C_3H_5)]_3PW_{12}O_{40}$ and $[(Ph_3P)_2Ir(H,D)_2]_3PW_{12}O_{40}$ Formed from Labeled Propylenes

	obsd (calcd),[a] %				
substrate	$(C_3H_5)Ir{-}H$	$(C_3H_5)Ir{-}D$	IrH_2	IrHD	IrD_2
$CD_3CH{=}CH_2$	58 (50)	48 (50)	43	44	13
$CH_3CD{=}CH_2$	78 (83)	22 (17)	96	4	0
$CH_3CH{=}CD_2$	67 (67)	33 (33)	84	16	0
c-C_3D_6	22 (0)	78 (100)	81	18	1

[a] Assuming statistical incorporation of substrate deuterons into the product.

Metathetical reaction of $[(Ph_3P)_2Ir(C_8H_{12})]PF_6$ with hydrated $(H_3O)_3PM_{12}O_{40}$ (M = Mo, W) in acetone provides pink $[(Ph_3P)_2Ir(C_8H_{12})]_3PMo_{12}O_{40}$ (1) and $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (2): $\delta(^{31}P)$ MAS 11, 5, −15; $E_b[Ir(4f_{7/2})]$ = 62.6 eV; λ_{max} (log ϵ) 388 (3.6), 478 (3.6), 572 (2.7) nm (DMSO).[3-6] Treatment of solid 1 or 2 with hydrogen at 1 atm quantitatively yields cyclooctane and pale yellow $[(Ph_3P)_2IrH_2]_3PMo_{12}O_{40}$ (3) and $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ (4): $\delta(^{31}P)$ MAS 30, −15; $E_b[Ir(4f_{7/2})]$ = 62.5 eV; surface area (N_2 adsorption) = 15.8 M^2 gm^{-1}.[6,7] Both 3 and 4 are insoluble in noncoordinating, nonreactive solvents. Dissolution in dimethylformamide produces $(Ph_3P)_2IrH_2(DMF)_2^+$ [$\delta(^1H)$ −27.8 (t, J_{PH} = 15 Hz); $\delta(^{31}P)$ 24.8]; because no hydrogen is evolved, it is improbable that 3 and 4 are dihydrogen complexes. Anion effects are already manifest for heterogeneous reduction of the BF_4^- or PF_6^- salts of $(Ph_3P)_2Ir(C_8H_{12})^+$ produces binuclear $(Ph_3P)_4Ir_2H_5^+$.[8,9]

Reduction of these derivatives of molecular metal oxide clusters parallels that of $[(Ph_3P)_2Ir(C_8H_{12})]PF_6$ in acetone which affords $[(Ph_3P)_2IrH_2(acetone)_2]PF_6$,[10] but here, it occurs in a solid–gas process in which no additional, coordinating solvents are present. Fourier transforms of the iridium L3 edge EXAFS spectrum of 3 provides a radial distribution function shifted by −0.1 Å relative to that of 1. The transform of the EXAFS of 3 displays a single

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(3) Hydrated $(H_3O)_3PW_{12}O_{40}$ was obtained from Alfa Products. ^1H NMR analysis indicates that 2 contains variable and up to 0.3 mol of acetone per $(Ph_3P)_2Ir(COD)^+$ unit. This zeolitic or lattice acetone has ν_{CO} 1708 cm^{-1} (Nujol), and it is not coordinated to iridium. In $[(Ph_3P)_2IrH_2(acetone)_2]PF_6$, ν_{CO} is 1664 cm^{-1}. When the hydrogenation of 2 is carried out in a pulsed reactor, it is seen that some of this acetone is released; the weak CO stretching band from residual acetone is not shifted. The IR spectra of 1–4 show no bands due to water.

(4) The −15 ppm signal is due to the $PW_{12}O_{40}^{3-}$ cluster. Splitting of the Ph_3P resonance is attributed to crystallographic nonequivalence of the $(Ph_3P)_2Ir(C_8H_{12})^+$ units: $\delta(^{31}P)$ (DMSO-d_6) 14.5, −14.5.

(5) Magic-angle spinning (MAS) and solution-phase chemical shifts are expressed relative to external $(CH_3)_4Si$ (^{13}C) or 85% H_3PO_4 (^{31}P). X-ray photoelectron binding energies, E_b, are referenced to the C(1s) line at 285.0 eV.

(6) Anal. Calcd for 1 (Found): C, 37.1 (36.8); H, 3.1 (2.9); Ir, 13.3 (13.0); Mo, 26.6 (27.0); P, 5.0 (4.9). Calcd for 2 (Found): C, 29.9 (29.4); H, 2.4 (2.3); Ir, 10.7 (10.3); P, 4.0 (4.1); W, 40.9 (39.9). Anal. Calcd for 3 (Found): C, 32.6 (32.5); H, 2.4 (2.5); Ir, 14.5 (14.7); Mo, 29.0 (29.3); P, 5.5 (5.7). Anal. Calcd for 4 (Found): C, 25.8 (25.8); H, 1.9 (2.1); Ir, 11.4 (11.7); P, 4.3 (4.6); W, 43.9 (42.8). The data are insensitive to small amounts of zeolitic solvent.

(7) 2: ^1H NMR (DMSO-d_6): δ 7.3–7.7 (m, Ph, 90 H), 4.31 (s, $=CH$, 12 H), 2.43 (d, CH_2, 12 H), 2.1 (s, $CH_3)_2CO$, 5.4 H), 2.03 (d, CH_2, 12 H); ^{13}C NMR (DMSO-d_6): δ 134.12 (C2,6), 131.09 (C4), 129.26 (d, 55, C1), 128.49 (C3,5), 86.21 (=CH), 30.47 (CH_2). X-ray powder pattern: strong lines at $d_{h,k,l}$ (I/I_0) 15.992 (100), 13.483 (37), 13.081 (31), 12.316 (30), 9.528 (46), 8.788 (48), 5.245 (33) Å.

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