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Photochemical Reactions of Bis(Bistrimethylsilylamido)tin(II) with Hexacarbonylmolybdenum and Tungsten

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Abstract

Irradiation of $M(CO)_6$ (M = Mo, W) and $Sn[N(SiMe_3)_2]_2$ in hexane with UV light results in carbonyl substitution to form both $M(CO)_5Sn[N(SiMe_3)_2]_2$ and $M(CO)_4(Sn[N(SiMe_3)_2]_2)_2$ complexes. The $M(CO)_4L_2$ species present the first examples in which both *cis* and *trans* isomers have been observed upon substitution of bulky divalent main group IV ligands. The highly air-sensitive $W(CO)_5L$ and $W(CO)_4L_2$ complexes have been isolated.

Introduction

The Lewis base behavior of divalent Ge, Sn, and Pb compounds containing bulky dialkyl or dialkylamide groups has been compared to that of tertiary phosphines when reactions with transition metal systems are considered [1]. However, some differences have been noted, such as the tendency of the main group IV ligands to displace only one carbonyl when irradiated in the presence of $M(CO)_6$ complexes (M = Cr, Mo, W). This contrasts with the more extensive substitution behavior of other bases and the common observance in these systems of *cis–trans* isomerism [2].

A few reports in which two carbonyls have been displaced have appeared but the picture they present is somewhat conflicting. While Lappert *et al.* [1] noted spectroscopic evidence for small amounts of *trans*-disubstituted products from irradiation of $Sn[CH(SiMe_3)_2]_2$ with $Cr(CO)_6$ and $Mo(CO)_6$, Veith *et al.* [3], using $Me_2Si(N\text{-}t\text{-}Bu)_2Sn$ under similar conditions, found *cis*-$Mo(CO)_4L_2$ to be the only disubstituted photolysis product. On the other hand, $Sn[N(SiMe_3)_2]_2$, a compound with analogous steric and electronic properties, was reported by Lappert to displace only one carbonyl from $W(CO)_6$ [4]. Having also had experience in the preparation of $Sn[N(SiMe_3)_2]_2$ [5], we would like to report the results of our photochemical studies of this ligand which include the observation of disubstituted *cis* and *trans* isomers.

Results and Discussion

The irradiation of an equimolar mixture of $Sn[N(SiMe_3)_2]_2$ and $W(CO)_6$ was monitored by infrared spectroscopy in the C≡O stretching region. A complex pattern of bands emerged with the spectrum, after 92 h, appearing as in Fig. 1. The reaction was stopped at this point due to extensive decom-

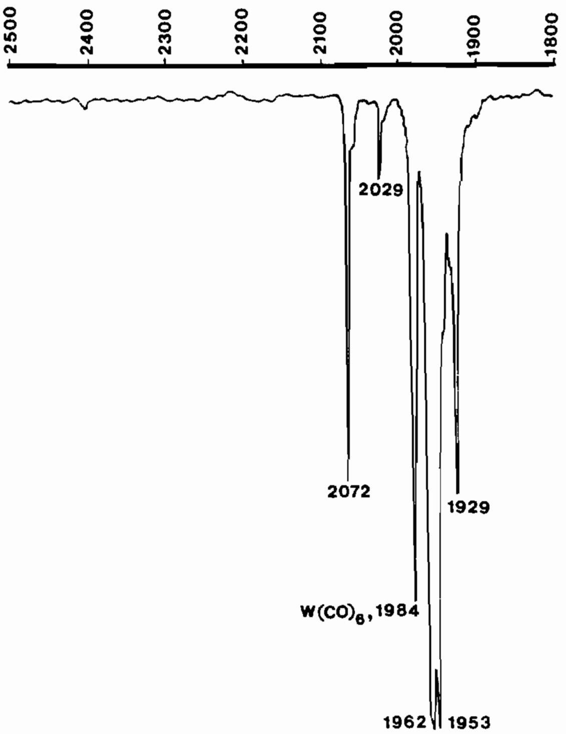

Fig. 1. $W(CO)_6 + Sn[N(SiMe_3)_2]_2$ after 92 hours.

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position, which resulted in the formation of insoluble brown particles. After filtration and a careful series of recrystallizations unreacted $W(CO)_6$ was removed and the mixture was separated into bright yellow and orange crystals having the individual spectra shown in Figs. 2 and 3, respectively. The pattern in Fig. 2 was that expected for an $M(CO)_5L$ system having local C_{4v} symmetry ($2A_1$ + E bands) and the assignment was supported by elemental analyses of the material (see Experimental). The orange crystals producing the spectrum in Fig. 3 gave analytical results consistent with the formula $M(CO)_4L_2$ but a definite structural assignment could not be made from the carbonyl pattern in Fig. 3. However another recrystallization of the material exhibited different relative carbonyl intensities (Fig. 4), revealing the absorption at 1929 cm^{-1} to be independent of the remaining pattern. On the basis of group theoretical considerations of *cis* and *trans* $M(CO)_4$ fragments a single band is predicted for the *trans* isomer while as many as four bands may be possible for the *cis* isomer. Thus the bands in Figs. 3 and 4 can be assigned to the two isomers as shown in Table I.

Irradiation of $Mo(CO)_6$ with $Sn[N(SiMe_3)_2]_2$ under the above conditions produced an infrared pattern resembling that of the tungsten reaction, with similar relative populations and bands shifted by only a few wavenumbers. Decomposition occurred more readily so that the reaction was stopped after 40 h with the spectrum appearing as in Fig. 5. Band assignments for $Mo(CO)_5Sn[N(SiMe_3)_2]_2$ and *cis* and *trans*-$Mo(CO)_4(Sn[N(SiMe_3)_2]_2)_2$ are listed in Table I. In view of the increased sensitivity of the molybdenum system and the difficulty encountered in separating the tungsten products, the individual molybdenum complexes were not isolated.

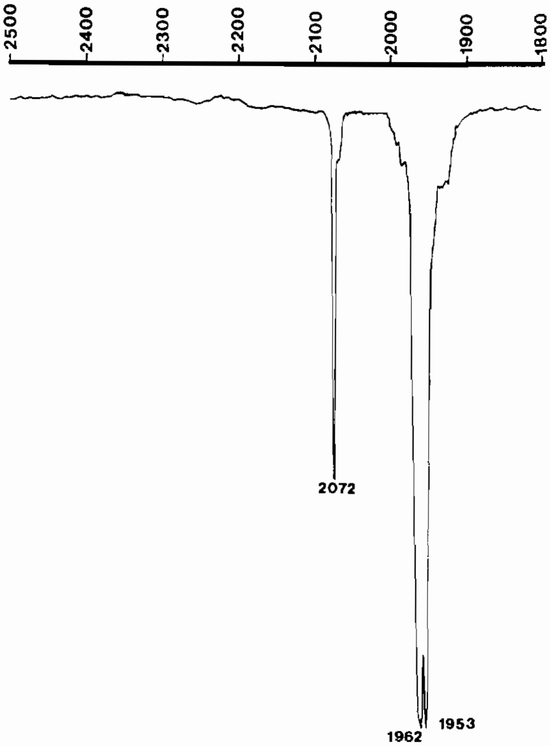

Fig. 2. $W(CO)_5Sn[N(SiMe_3)_2]_2$.

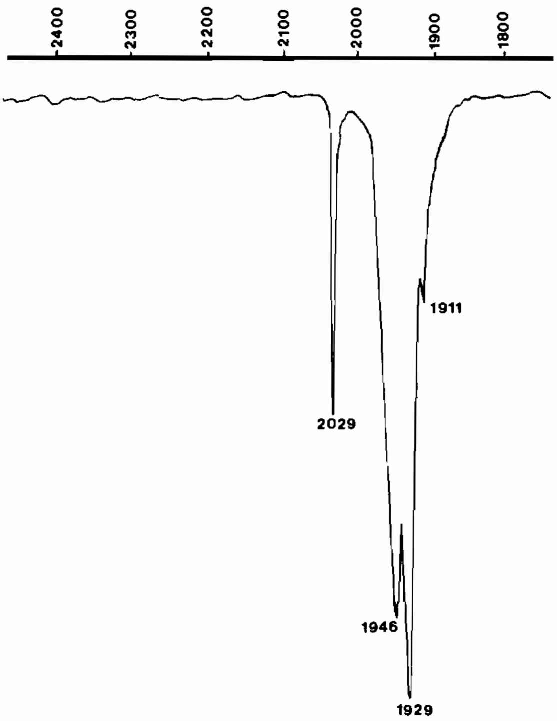

Fig. 3. *cis* and *trans*-$W(CO)_4(Sn[N(SiMe_3)_2]_2)_2$ (first recrystallization).

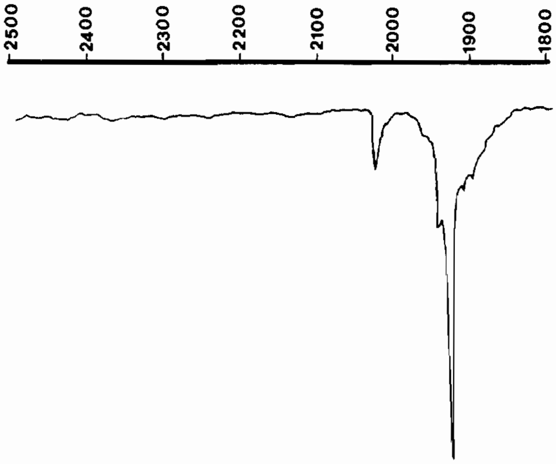

Fig. 4. *cis* and *trans*-$W(CO)_4(Sn[N(SiMe_3)_2]_2)_2$ (second recrystallization).

TABLE I. Infrared Spectra in C≡O Stretching Region[a].

Compound	W ν(C≡O)	Mo ν(C≡O)
M(CO)$_5$Sn[N(SiMe$_3$)$_2$]$_2$	2072s 1962vs 1953vs	2074s 1970vs 1961vs
trans-M(CO)$_4$(Sn[N(SiMe$_3$)$_2$]$_2$)$_2$	1929	1937
cis-M(CO)$_4$(Sn[N(SiMe$_3$)$_2$]$_2$)$_2$	2029m 1946s 1911sh	2033m 1950s 1919sh

[a] Spectra recorded in n-hexane.

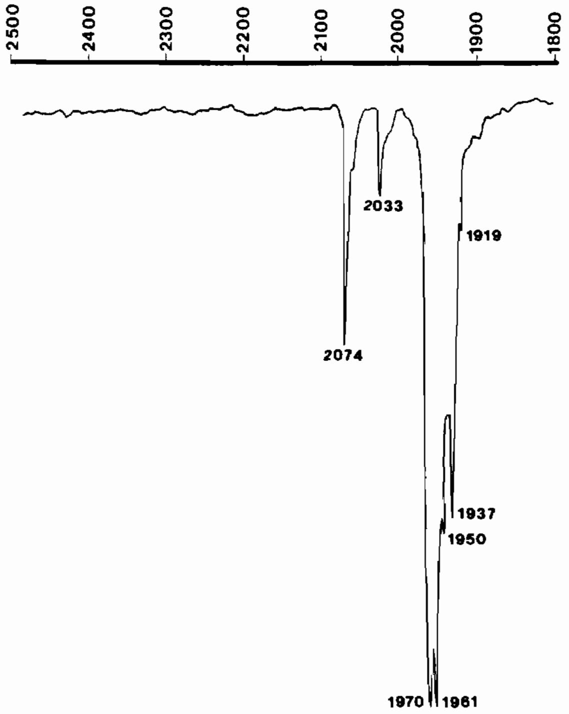

Fig. 5. Mo(CO)$_6$ + Sn[N(SiMe$_3$)$_2$]$_2$ after 40 hours.

While differences between the photolysis results described above and earlier studies may have been due to aspects of the irradiation conditions, closer examination suggests that in several cases disubstituted *cis* and/or *trans* isomers may have been overlooked. For example, the infrared spectrum reported for W(CO)$_5$Sn[N(SiMe$_3$)$_2$]$_2$ contains four carbonyl bands [4] (one more than allowed by local C_{4v} symmetry) only three of which correlate with those in Table I. The fourth, reported to be at 1931 cm^{-1}, is clearly absent from the spectrum in Fig. 2, but matches almost exactly that of *trans*-W(CO)$_4$(Sn[N(SiMe$_3$)$_2$]$_2$)$_2$. This suggests a result similar to that of the M(CO)$_6$/Sn[CH(SiMe$_3$)$_2$]$_2$ irradiation where infrared evidence of the *trans* isomer was also seen [1]. However in each of these situations overlap of all but the relatively weak band in the 2030 region would make detection of the *cis* isomer extremely difficult without separation of M(CO)$_5$L. When this was achieved, as in the Me$_2$Si(N-t-Bu)$_2$Sn complexes, the infrared spectrum, recorded in benzene, was cited as evidence of only the *cis* isomer [3]. However, the reported spectrum, consisting of a sharp band at 2010 cm^{-1} and a broad band at 1918 cm^{-1}, does not rule out the presence of the *trans* isomer as a constituent of the lower wavenumber band. This type of pattern is exactly what we observed when the spectrum in Fig. 3 was run in several solvents other than hexane. Substitution of more than one carbonyl and the formation of *cis* and *trans* isomers is thus likely to be a more general characteristic of the bulky divalent group IV systems with the result that their Lewis-base behavior toward transition metal systems is even more similar to that of main group V systems than had been previously thought.

Experimental

All reactions were conducted under an atmosphere of prepurified nitrogen or argon using a positive-pressure dry box or an Ace-Burlitch Inert Atmosphere System with Schlenk techniques. Pentane and hexane were dried, distilled over sodium, and subsequently degassed using three freeze-pump-thaw cycles prior to use. Both W(CO)$_6$ and Mo(CO)$_6$, obtained from Strem Chemicals, were purified by sublimation. The amide ligand, Sn[N(SiMe$_3$)$_2$]$_2$, was prepared by reported methods [5, 6].

The infrared spectra of the reaction mixtures and the resulting crystals were measured in the 2500–1600 cm^{-1} range on a Perkin-Elmer 283 spectrometer calibrated with gaseous DCl. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The techniques employed for obtaining samples for these two measurements were those described by Gibson and Hsu [7]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Reaction of W(CO)$_6$ with Sn[N(SiMe$_3$)$_2$]$_2$

Equimolar amounts (0.012 mol) of hexacarbonyltungsten and Sn[N(SiMe$_3$)$_2$]$_2$ were dissolved in 125 ml of n-hexane. The reaction mixture was prepared in a photolysis vessel in the dry box after which it was removed and connected to the inert atmosphere system. The solution, cooled by a circulating water jacket, was irradiated with a 250W General Electric sunlamp filtered through pyrex for 92 h at which time the irradiation process was terminated. The irradiation mixture was filtered into a Schlenk reaction vessel and reduced to dryness. The reaction residue was then dissolved in 20 ml pentane and filtered through celite into a low-volume crystallizer. Using dry ice/i-propanol in the outer jacket, unreacted $W(CO)_6$ was precipitated out. This process was repeated twice after which a slow lowering in temperature under reduced pressure caused orange/yellow crystals to precipitate. Using cold, degassed n-pentane, the orange/yellow crystals were recrystallized three successive times, yielding yellow $W(CO)_5Sn[N(SiMe_3)_2]_2$ (~3.1 g, 34%), m.p. 86 °C [Found: C, 26.43; H, 4.78; N, 3.51. Calc'd for $C_{17}H_{36}WN_2O_5Si_4Sn$: C, 26.74; H, 4.76; N, 3.67]. The mother liquors obtained from the first two recrystallizations contained orange $W(CO)_4(Sn[N(SiMe_3)_2]_2)_2$ which precipitated after 48 h at –10 °C (~1.5 g, 11%), m.p. 159–160 °C [Found: C, 29.52; H, 5.70; N, 4.66. Calc'd for $C_{28}H_{72}WN_4O_4Si_8Sn_2$: C, 28.62; H, 6.18; N, 4.77].

Reaction of $Mo(CO)_6$ with $Sn[N(SiMe_3)_2]_2$

In the same manner as above, equimolar amounts of $Mo(CO)_6$ and $Sn[N(SiMe_3)_2]_2$ were irradiated in n-hexane for 40 hours. Following filtration and reduction of solvent volume, $Mo(CO)_6$ was removed by successive crystallizations until a small amount of a yellow/orange material, free of $Mo(CO)_6$, and having the infrared spectrum in Fig. 5 was obtained. Further separation of the products was not attempted.

Acknowledgements

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