

Figure 1. Carbonyl stretching frequencies of  $[\text{IrCOCl}(\text{PPh}_3)_2]$  and its adducts vs. electron affinity of added ligand. Except for the  $\text{BF}_3$  adduct all infrared data are taken from the literature.<sup>10,12</sup> The molecular electron affinities for  $\text{O}_2$ ,  $\text{SO}_2$ , and  $\text{BF}_3$  are those reported by V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold, London, 1966. For TCNE the value is from G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

$[\text{IrClCO}(\text{P}(\text{C}_6\text{H}_5)_3)_2]$  and its bis(boron trifluoride) adduct.<sup>7</sup> However, formation of the 1:1 complex in solution is clearly indicated by titrations in which composition of the benzene solution is monitored by infrared or near-ultraviolet spectroscopy. At a composition of 1.2 $\text{BF}_3$ :1Ir complex the 1968- $\text{cm}^{-1}$  band of the parent complex has disappeared and a single new CO stretching frequency has taken its place at 2067  $\text{cm}^{-1}$ . When the reaction is followed under experimentally more favorable conditions (dilute solution at 387  $\mu\text{m}$ ), the mole ratio at the end point is much closer to 1:1 (1 $\text{BF}_3$  per 1.021). The molecular weight of the 1:1 adduct, as indicated by cryoscopy in benzene solution, is 900 vs. the formula weight of 848. Thus, although a 1:1 complex is formed in solution, it appears to disproportionate upon removal of solvent.

In view of the molecular weight and CO stretching frequency, the two most likely modes of attachment of  $\text{BF}_3$  to the Ir complex for 1:1 adduct are (1) simple Ir-B donor-acceptor interaction or (2) oxidative insertion of the Ir atom into a B-F bond.<sup>8</sup>

The former possibility is favored because (1) there is evidence against oxidative insertion in the case of the 2:1 adducts (*i.e.*, no trigonally bonded boron is present), (2) the parent complex, **1**, can be regenerated by treating the adduct with mild bases such as acetone or amines, and (3)  $\text{B}(\text{C}_6\text{F}_5)_3$ , which is similar in acidity to  $\text{BF}_3$ <sup>9</sup> but for which insertion is unlikely, forms a weak adduct with  $[\text{IrClCO}(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ . This adduct displays a CO stretching frequency similar to that of the  $\text{BF}_3$  adduct. (Furthermore, the more stable  $[\text{IrClCO}(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2] \cdot \text{B}(\text{C}_6\text{F}_5)_3$  yields a  $^{19}\text{F}$  nmr spectrum which is characteristic of a simple  $\text{B}(\text{C}_6\text{F}_5)_3$  adduct and not an insertion product.) Since the CO stretching frequencies are nearly identical for the 1:1 and 2:1 adducts, it is probable that the second molecule of  $\text{BF}_3$  is not attached directly to Ir, but the true nature of the 2:1 adduct is not clear.

(7) Solvent removal was performed on the vacuum line which allowed a check of all volatiles removed from the reaction mixture. This experiment demonstrated that no  $\text{BF}_3$  was evolved from the 1:1 mixture.

(8) G. Schmid, W. Arloth, and H. Nöth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 696 (1967).

(9) A. G. Massey and A. G. Park, *J. Organometal. Chem.* (Amsterdam), **5**, 218 (1966).

In Figure 1 the carbonyl stretching frequencies of several molecular adducts and the uncoordinated iridium(I) complex are plotted as a function of the electron affinity of the added molecule.<sup>10</sup> There is a roughly linear dependence of the stretching frequency upon the electron affinity indicating that the electron density around the iridium atom decreases in a smooth continuous fashion rather than in discrete discontinuous jumps between the formal oxidation states I, II, and III.

It has been pointed out<sup>11-13</sup> that  $\text{O}_2$ ,  $\text{C}_2(\text{CN})_4$ , and  $\text{SO}_2$  can form bonds to iridium in which two types of interactions can occur. These are weak donation from filled  $\pi$  orbitals in  $\text{O}_2$  and  $\text{C}_2(\text{CN})_4$  or the nonbonding electron pair on the sulfur atom in  $\text{SO}_2$ , and moderately strong acceptance of electron density from the metal by a  $\pi$ -bonding interaction of filled metal d orbitals and antibonding orbitals on the ligand molecules. In the case of the boron trifluoride adduct, the only possible interaction is  $\sigma$  donation from iridium to boron. The correlation of the carbonyl stretching frequencies with molecular electron affinities for the added molecules, including  $\text{BF}_3$ , suggests that all of the molecular adducts considered here may be viewed as Lewis salts in which the metal primarily serves as a donor. Accordingly, much of the chemistry of the Ir(I) adducts can be described in terms of the strongest electron acceptor (Lewis acid) forming the most stable complex. Thus, the uptake of  $\text{O}_2$  and of  $\text{SO}_2$  by  $[\text{IrClCO}(\text{P}(\text{C}_6\text{H}_5)_3)_2]$  is reversible, while  $\text{BF}_3$  uptake is not. Similarly,  $\text{C}_2\text{F}_4$  is more strongly<sup>14</sup> held than  $\text{C}_2\text{H}_4$ . However, some caution is necessary in the inference of Lewis acid strengths from known or estimated electron affinities, or even from acidity toward radically different reference bases. For one thing the three-center bonds formed between the oxygen-like acids and the metal are different in detail from the two-center boron-metal bond. Also differences may occur in the geometry of the first coordination sphere and in the degree of reorganization of the acid. Therefore, comparisons of stabilities with electron affinities or of frequencies with electron affinities are only potentially meaningful for large differences.<sup>15</sup>

(10) It is to be emphasized that upon interaction with the iridium complex, cleavage of the added molecule does not occur for any of the cases cited in Figure 1.

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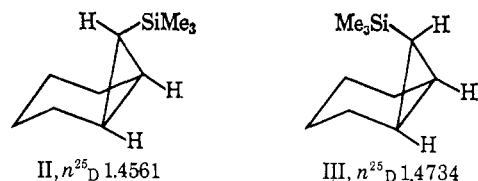
## Trimethylsilyldiazomethane and Trimethylsilylcarbene

Sir:

A recent report on "trimethylstannyldiazomethane"<sup>1</sup> mentioned in passing that trimethylsilyldiazomethane



pounds by Chvalovský, *et al.*<sup>7</sup> Such CuCl-catalyzed decomposition of  $\text{Me}_3\text{SiCHN}_2$  in benzene in the presence of an excess of cyclohexene gave as the major product (in 65% yield) *anti*-7-trimethylsilylnorcarane (II). Three minor products were the other 7-trimethylsilylnorcarane isomer (III) (7%), *trans*-1,2-bis(trimethylsilyl)ethylene (13%), and the *cis* isomer (9%). All products were isolated as pure materials by glpc. The identification of the 7-trimethylsilylnorcarane iso-



mers was based on their analyses and their infrared and nmr spectra. Particularly the latter were of value: in the nmr spectrum (in  $\text{CCl}_4$ ) of II, the  $\text{Me}_3\text{Si}$  group appeared as a singlet at  $\tau$  10.09 and the cyclopropane proton *gem* to the trimethylsilyl group as a triplet at  $\tau$  10.69 ( $J = 7$  cps). In III these resonances were seen at  $\tau$  9.88 and 10.41 (triplet,  $J = 10$  cps). In support of these assignments we may note that previous work has established that in norcaranes the 7-proton *syn* to the  $-(\text{CH}_2)_4-$  bridge is more highly shielded than is the proton which is *anti* to the tetramethylene bridge and, furthermore, that the magnitude of *cis* coupling between vicinal protons in cyclopropanes is greater than that of *trans* coupling.<sup>8</sup> The CuCl-catalyzed decomposition of trimethylsilyldiazomethane in the presence of an excess of *cis*-4-methyl-2-pentene gave, in addition to *trans*- and *cis*-1,2-bis(trimethylsilyl)ethylenes, the two isomers of 1-methyl-2-isopropyl-3-trimethylsilylcyclopropane. Further carbenoid reactions of trimethylsilyldiazomethane are under investigation.

In conclusion, it should be noted that trimethylsilylcarbene has been proposed as an intermediate previously: in the  $\text{Me}_3\text{SiCHCl}_2 + \text{Na-K}$  gas phase reaction (which gave  $\text{Me}_2\text{HSiCH}=\text{CH}_2$ ),<sup>9</sup> in the rather complicated reaction of  $\text{Me}_3\text{SiCH}_2\text{Cl}$  with lithium,<sup>10</sup> and in the reaction of  $\text{Me}_3\text{SiCH}_2\text{Cl}$  with *n*-butyllithium.<sup>11</sup> The latter reaction was carried out in the presence of cyclohexene, but no 7-trimethylsilylnorcarane was obtained. More recently, a brief report concerning trimethylsilylcarboethoxycarbene has appeared.<sup>12</sup>

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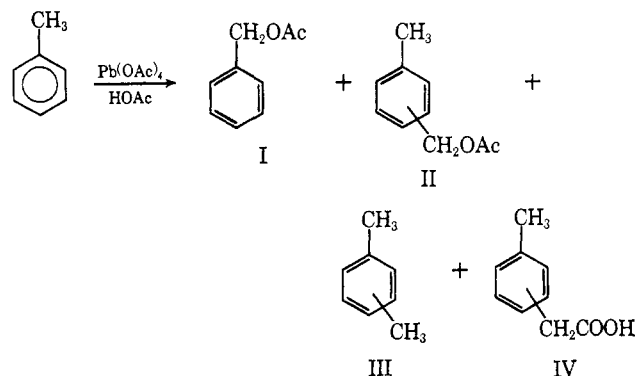
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## Oxidation by Metal Salts. I. The Reaction of Lead Tetraacetate with Toluene

Sir:

Despite many investigations of the oxidation of alkylaromatics by lead tetraacetate, the mechanisms of these processes are not fully understood, and some conflicting theories and interpretations are current in the literature.<sup>1</sup> In particular, the formation of products in which the  $-\text{CH}_2\text{OAc}$  group has been added to the aromatic ring has been observed in a few instances<sup>2</sup> and the mechanism of their formation has not been adequately explained. We wish to report our studies on the oxidation of toluene by lead tetraacetate and present a general mechanism which explains the production of these adducts and predicts the conditions conducive to their formation.

The oxidation of toluene with lead tetraacetate in refluxing acetic acid containing anhydrous potassium acetate under a nitrogen atmosphere<sup>3</sup> yielded two major products, benzyl acetate (I) and methylbenzyl acetate (II) (mixture of isomers, predominantly *ortho*), along with minor amounts of xylenes (III) and tolylacetic acids (IV).



In a typical experiment in which 21.7 mmoles of lead tetraacetate was added to a solution of toluene (15-fold excess) in acetic acid, the following product yields were obtained: benzyl acetate (7.04 mmoles), methylbenzyl acetates (4.95 mmoles), xylenes (1.91

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(3) In the presence of oxygen, the reaction times increased and the yields of products based on lead tetraacetate consumed decreased, as would be expected in a radical chain process. These observations are in accord with those reported by Davidson and Triggs.<sup>2d</sup>