found to be consistent with the STO-3G calculated structure. Complete assignments including the weaker a-type rotational transitions will probably require enriched samples.

In the rigid rotor approximation, a molecule, with all atoms in the A-B plane, has a value of $I_c - I_a - I_b = 0$. For molecules with light atoms out of plane, the value of $I_c - I_a - I_b$ indicates the amount of mass out of plane. The assumed 2*H*-azirine structure has two hydrogen atoms out of plane as do the closely related molecules cyclopropene and diazirine. $I_c - I_a - I_b$ for 2*H*-azirine is −3.383 amu Å^2 whereas for the latter two molecules, −3.333 and −3.478 amu Å^2 were obtained.[6,7]

All of the above evidence obtained from the microwave spectrum is consistent with the proposed cyclic structure of 2*H*-azirine. The stability of the compound is somewhat greater than initially expected as it can be trapped at liquid nitrogen temperature and revaporized. Decomposition to acetonitrile apparently occurs in benzene and cyclohexane solution thus far preventing observation of its NMR spectrum.

Photolysis of vinyl azide in the same apparatus with the addition of a 450-W Hanovia 379A36 mercury lamp resulted in a very small yield of 2*H*-azirine along with acetonitrile, propionitrile, and ammonia.

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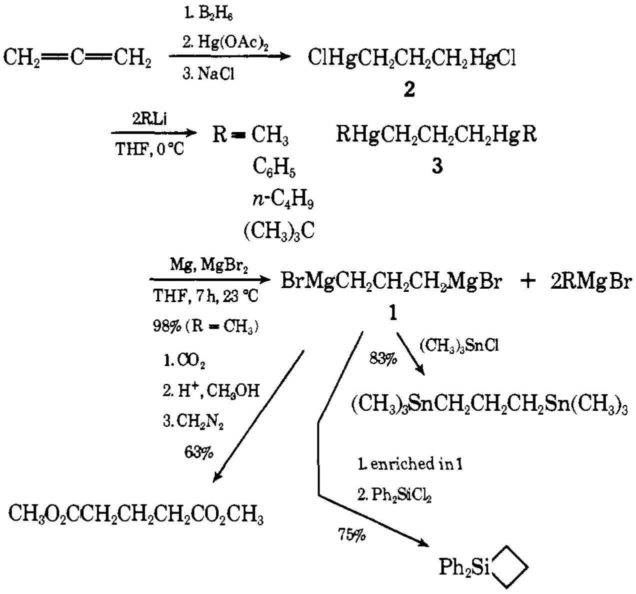
Propane-1,3-di(magnesium halide)[1]

Sir:

Metallocyclic compounds are intermediates in a number of interesting metal-catalyzed reactions.[2] A useful method for preparing authentic metallocycles having rings of five or more members for mechanistic studies is the reaction of a metal halide with an alkane-α,ω-dimagnesium or -dilithium reagent. It has not been possible to prepare four-membered metallocycles—metallocyclobutanes—by this procedure, since the requisite dimagnesium or dilithium reagents have not been available: reaction of 1,3-dihalopropanes with magnesium or lithium yields primarily cyclopropane, and does not generate propane-1,3-dimetal compounds.[3,4] We report here a preparation of propane-1,3-di(magnesium halide) (**1**), and illustrate its usefulness in the preparation of metallocyclobutanes by syntheses of 1,1-dimethyl- and 1,1-diphenylsilacyclobutane (Scheme I).

Hydroboration-mercuration[5] of allene gave propane-1,3-di(mercury(II) chloride) (**2**). Attempts to convert **2** directly to **1** by transmetalation[6] with magnesium, or to propane-1,3-dilithium by reaction with lithium, produced only an unreactive, insoluble mixture of polymeric dialkylmercury compounds. To prevent the formation of these compounds on exposure of the propane-1,3-dimercury(II) moiety to magnesium, **2** was first treated with 2 equiv of an organolithium reagent, RLi, and converted to *soluble* dialkylmercury reagents (**3**).[7,8] Treatment of **3** with magnesium powder in THF containing magnesium bromide (prepared in situ by reaction of magnesium with 1,2-dibromoethane) yielded a mixture of **1** and monofunctional organomagnesium reagents, RMgX.

Scheme I. Preparation, Isolated Yields, and Reactions of Propane-1,3-di(magnesium halide) (1) and Related Compounds



The composition of these mixtures of organomagnesium reagents was assayed by addition of an excess of trimethyltin chloride, and GLC examination of the resulting organotin compounds. In a typical reaction sequence carried through using methyllithium to convert **2** to **3** (R = CH_3), the organotin compounds detected were (GLC yields, %, based on **2**): $(CH_3)_3SnCH_2CH_2CH_2Sn(CH_3)_3$ (98), $(CH_3)_4Sn$ (100), $CH_3CH_2CH_2Sn(CH_3)_3$ (2), $CH_2{=}CHCH_2Sn(CH_3)_3$ (<1). Control experiments established that the conditions used in these assays converted n-decylmagnesium bromide to n-decyltrimethyltin quantitatively. The presence of **1** was confirmed by isolation of dimethyl glutarate in 63% yield following carbonation and esterification, and by preparation of 1,1-dimethylsilylcyclobutane in 66% yield (GLC), and 1,1-diphenylsilylcyclobutane in 75% yield (isolated) following reaction with the appropriate diorganosilicon dihalides (Scheme I).[9]

The unsymmetrical dialkylmercury compounds (**3**) could be isolated. For preparative reactions, however, isolation was not necessary: when a suspension of 1.0 equiv of **2** and 30 equiv (a large excess) of magnesium powder in THF was treated in sequence with 2.0 equiv of an organolithium reagent and 2.0 equiv of 1,2-dibromoethane, and the resulting mixture allowed to stir for 7 h at room temperature, **1** was generated in yields that depended on the structure of the organolithium reagent used (yield of **1**, %, based on **2**): CH_3Li (98), C_6H_5Li (95), n-C_4H_9Li (80), $(CH_3)_3CLi$ (60). For most preparative work, **3** (R = CH_3) was the most convenient material with which to work. The preparation of **1** by this procedure is necessarily accompanied by the formation of 2 equiv of monofunctional Grignard reagent (RMgX). For further reactions with monofunctional substrates, use of this mixture presented little difficulty, since the products were easily separated. For metallocyclobutane formation, however, it was desirable to use a solution of **1** which contained less RMgX. Two techniques produced solutions which were enriched in **1**. In the first, addition of diethyl ether to the reaction mixture in THF resulted in the separation into two phases, with **1** concentrated in the lower. Removal of the upper layer, solution of the lower layer in THF, and repetition of this procedure several times resulted in solutions in which the ratio of **1** to RMgX was greater than 9:1. A disadvantage of this procedure is that only 10–20% of the available **1** is recovered. The second procedure involved treating the initially formed mixture of organomagnesium reagents with additional **1** and subsequent transmetalation of the resulting mixture of diorganomercury compounds. With this method 30-mmol quantities of **1** can be prepared routinely in solutions in which the ratio of **1** to RMgX is ca. 2:1. Attempts to produce more homogeneous solutions of **1** with this process are frustrated by increasingly slow transmetalation rates and decreased yields of **1**.[10] Utilization of these two techniques in combination permits the preparation of useful quantities (5–10 mmol) of **1** in solutions containing no more than ca. 20 mole % of this quantity of monofunctional Grignard reagents.

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Supplementary Material Available. Experimental procedures for the preparation of **1** and **2** (4 pages). Ordering information available on any current masthead page.

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(10) Thermal instability apparently limits the length of time that solutions of **1** can be manipulated without decrease in purity. Qualitative observation suggests that storage of **1** in THF at ambient temperature for 7 days converts ca. 50% of it to a mixture of allyl- and *n*-propylmagnesium halides.

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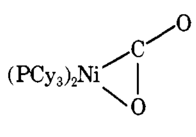
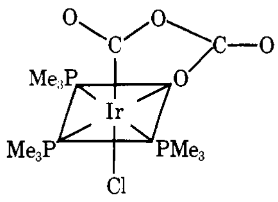
Carbon Dioxide Coordination Chemistry. 3.[1] Adducts of CO_2 with Iridium(I) Complexes

Sir:

The present concern about alternate petrochemical feedstocks has heightened interest in the chemistry of carbon dioxide. One area under active consideration involves CO_2 activation via coordination to a transition metal complex.[2] Several adducts of CO_2 have been claimed and two of these have been characterized crystallographically (**1**[3] and **2**[1b]). We report the preparation and properties of the novel family of adducts $[IrL_4]Cl{\cdot}CO_2$, L = trialkylphosphine or -arsine.



I



2

A representative adduct is formed from the highly reactive orange complex $[Ir((CH_3)_2PCH_2CH_2P(CH_3)_2)_2]Cl$ ($[Ir(dmpe)_2]Cl$)[4] which is formed upon reaction of $Ir_2Cl_2(cyclooctene)_4$ with 2 equiv of dmpe.[5] When a suspension of $[Ir(dmpe)_2]Cl$ in benzene is pressured to 1 atm of CO_2 at room temperature, the orange solid is bleached white within seconds. The same white solid is obtained from suspensions in other hydrocarbons or ethers, from benzonitrile solution or with dry $[Ir(dmpe)_2]Cl$. The total elemental analysis of the resultant white solid indicates the stoichiometry $Ir(dmpe)_2Cl{\cdot}CO_2$ (**3**).[6] **3** dissolves in acetonitrile, acetone, or methylene chloride with liberation of the CO_2. Treatment with HCl or thermal decomposition of the solid at 200 °C also causes CO_2 evolution. The bound CO_2 may be displaced by various small molecules (L) to yield $[Ir(dmpe)_2(L)]Cl$[5] (L = CO, PMe_3, CS_2) or *cis*-$[Ir(H)_2(dmpe)_2]Cl$[5] (L = H_2). The above properties suggest that the bound CO_2 functions as a discrete ligand. Attempts at solution characterization have not been successful.

$Ir(dmpe)_2Cl{\cdot}CO_2$, **3**, displays two strong IR bands due to the bound CO_2 at 1550 and 1230 cm^{-1}, as confirmed by isotope labeling.[7] Heating a solution or suspension of this adduct at $\sim$120 °C in a closed system transforms it to a solid with the same C, H, O analyses but with IR bands at 2180 and 1640 cm^{-1} replacing those mentioned above. Isotope labeling affords IR bands at 2180 and 1622 cm^{-1} with $C^{18}O_2$ and at 2180 and 1600 cm^{-1} with $^{13}CO_2$. The 2180-cm^{-1} band is assigned to ν_{Ir-H} consistent with various other iridium(III) hydrides.[8,9] The IR band at 1640 cm^{-1}, shown to be due to the bound CO_2, is assigned to $\nu_{C=O}$ of a monodendate carboxylate.[10] Thus the above data suggest that a coordinated dmpe has been metalated and carboxylated. The simplest formulation of this transformation is:

$$\underset{\mathbf{3}}{\mathrm{Ir(dmpe)_2Cl{\cdot}CO_2}} \xrightarrow[\text{heat}]{} [\mathrm{I}\underbrace{\mathrm{r(H)(Me(CH_2CO_2}}\mathrm{)PC_2H_4PMe_2)(dmpe)]Cl}$$

Whether this product is mononuclear and what its structure is are not yet known. Interestingly, in the absence of CO_2, metalation is not observed. Apparently, as reported for other systems,[1a] carboxylation is more favorable than metalation alone. The enhanced stability may be due to the increased size of the metallocycle.

CO_2 forms adducts like **3** with other complexes. Thus the orange $[Ir(diars)_2]Cl$[5] (diars = *o*-phenylenebis(dimethylarsine)) readily binds 1 equiv of CO_2 with concomitant bleaching of the orange complex and development of strong new IR bands at 1550 and 1220 cm^{-1}. Increasing the ligand bulk attenuates $[IrL_4]^+$ reactivity toward CO_2 and other small molecules such that, in contrast to $[Ir(dmpe)_2]Cl$, the complex $[Ir(Et_2PC_2H_4PEt_2)_2]Cl$[4] binds and retains CO_2 only at $\gtrsim 3$ atm CO_2 pressure. The corresponding rhodium complexes react with difficulty with CO_2, suggesting that metal basicity is an important prerequisite to CO_2 adduct formation.

The CO_2 derived IR bands of these one to one adducts should be contrasted with the 1740 and 1150 cm^{-1} bands of **1**.[3] The different IR spectra imply significantly different