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.

Acknowledgment. We thank Drs. Cathy Costello and Klaus Biemann for GLC-mass spectra, and Mr. Michael Richard for assistance with other mass spectra.

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

References and Notes

(1) Supported by the National Science Foundation, Grant MPS74-20946.

(2) For recent references, see T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **98**, 2519 (1976); J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **98**, 6521 (1976); J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *ibid.*, **98**, 6529 (1976); R. H. Grubbs, P. L. Burk, and D. D. Carr, *ibid.*, **97**, 3265 (1975); C. P. Casey and T. J. Burkhardt, *ibid.*, **96**, 7808 (1974); E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975); R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *J. Am. Chem. Soc.*, **97**, 812 (1975).

(3) (a) E. Mueller, Ed., "Methoden der Organischen Chemie" (Houben-Weyl), Vol. 13/2a, Georg Thieme Verlag, Stuttgart, 1973, pp 97–106; (b) I. T. Millar and H. Heaney, *Q. Rev., Chem. Soc.*, **11**, 109 (1957); (c) M. S. Kharasch ad O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice Hall, New York, N.Y., 1954, pp 34 –35; (d) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

(4) A patent claim for the formation of 1,3-dilithiopropane from 1,3-dichloropropane and lithium metal is based only on a low yield of titratable organolithium reagent, and contained no evidence for the formation of dilithium reagent: K. C. Eberly, U.S. Patent 2 947 793 (1960); *Chem. Abstr.*, **55**, 382 (1961).

(5) H. C. Brown and R. C. Larock, *J. Am. Chem. Soc.*, **92**, 2467 (1970).

(6) (a) Reference 3a, Vol 13/2b, 1974, pp 277–281; (b) Reference 3a, pp 202–205; (c) F. R. Jensen and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 1004 (1960).

(7) *CAUTION:* Although we have not explicitly checked for volatile alkylmercury species in these reactions, disproportionation of compounds **3** will certainly generate them. All reactions involving organomercury compounds should be conducted in a good hood, and contact with solutions or vapor avoided.

(8) Reference 6a, pp 234–236.

(9) Silacyclobutane chemistry has been reviewed by R. Damrauer, *Organomet. Chem. Rev., Sect. A*, **8**, 67 (1972).

(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.

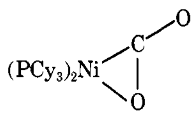
Lawrence C. Costa, George M. Whitesides*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts, 02139

Received July 14, 1976

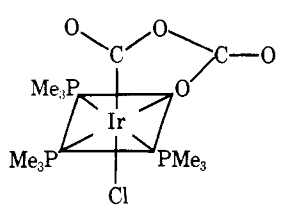
Carbon Dioxide Coordination Chemistry. 3.[1] Adducts of CO_2 with Iridium(I) Complexes

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.



1



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.

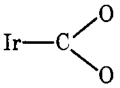
$Ir(dmpe)_2Cl\cdot CO_2$, **3**, displays two strong IR bands due to the bound CO_2 at 1550 and 1230 cm^{-1}, as confirmed by isotope labeling.[7] Heating a solution or suspension of this adduct at ~120 °C in a closed system transforms it to a solid with the same C, H, O analyses but with IR bands at 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:

$$\underset{\mathbf{3}}{\mathrm{Ir(dmpe)_2Cl\cdot CO_2}} \xrightarrow[\text{heat}]{} [\mathrm{I}\underbrace{\mathrm{r(H)(Me(CH_2CO}}\mathrm{_2)PC_2H_4PMe_2)(dmpe)]Cl}$$

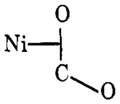
Whether this product is mononuclear and what its structure is are not yet known. Interestingly, in the absence of CO_2, metalation is not observed. Apparently, as reported for other systems,[1a] carboxylation is more favorable than metalation alone. The enhanced stability may be due to the increased 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 structures for **1** and for **3** and its congeners. The latter adducts may contain



configurations rather than the



grouping of **1**. Further research on the nature and reactivity of CO_2 adducts is in progress.

Acknowledgment. The author appreciates suggestions by Dr. G. W. Parshall concerning the interaction of CO_2 with transition metal complexes, and thanks Drs. Parshall and U. Klabunde for useful discussions.

References and Notes

(1) (a) Part 2, A. D. English and T. Herskovitz, *J. Am. Chem. Soc.*, in press; (b) part 1, T. Herskovitz and L. J. Guggenberger, *ibid.*, **98**, 1615 (1976).
(2) Two recent reviews are: (a) M. E. Vol'pin and I. S. Kolomnikov in "Organometallic Reactions", Vol. 5, E. I. Becker and M. Tsutsui, Ed., Wiley, New York, N.Y., 1975, pp 313–386; (b) T. Ito and A. Yamamoto, *J. Soc. Org. Synth. Chem., Tokyo*, **34**, 308–318 (1976).
(3) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 636 (1975).
(4) $[Ir(dmpe)_2]Cl$ forms one to one adducts with various small molecules (e.g., C_2H_4, CO, CS_2, PMe_3). The molecules HA, A = H, Cl, O_2CCH_3, CH_2CN,[1a] etc., oxidatively add to $[Ir(dmpe)_2]Cl$ yielding *cis*- and *trans*-$[Ir(H)(A)(dmpe)_2]Cl$.
(5) T. Herskovitz, to be submitted for publication.
(6) Calcd for $C_{13}H_{32}O_2P_4ClIr$: C, 27.30; H, 5.64; O, 5.60; P, 21.66; Cl, 6.20; Ir, 33.60. Found: C, 27.65; H, 5.76; O, 5.42; P, 21.56; Cl, 6.44; Ir, 33.29.
(7) With $^{13}CO_2$ these bands are at 1515 and 1220 cm^{-1} while with $C^{18}O_2$ they are at 1530 and 1200 cm^{-1}; IR data are from Nujol mulls.
(8) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(9) A. D. English and T. Herskovitz, manuscript in preparation.
(10) S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, **11**, 660 (1972).

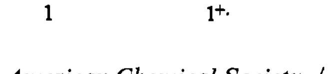
T. Herskovitz
Contribution No. 2453, the Central Research and Development Department
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received December 6, 1976

Isolation of 9,9′-Bis-9-azabicyclo[3.3.1]nonane Radical Cation Hexafluorophosphate, and Its Reversible Oxidation to the Dication

Sir:

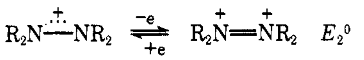
Cyclic voltammograms for the oxidation-reduction of many tetraalkylhydrazines (**1**) show the wave shape expected for nearly reversible (rapid) electron transfer at room temperature, allowing convenient determination of the standard oxidation potential, E_1^0, for these compounds.[1] Deprotonation of $\mathbf{1}^{+\cdot}$ would lead to its destruction, since the resulting α-hydrazinoalkyl radical would be more easily oxidized than **1**. Proton loss from $\mathbf{1}^{+\cdot}$ is clearly far slower than from alkylamine radical cations; alkylamines show irreversible cyclic voltammograms, attributed to rapid deprotonation of the radical cation.[2] Although many tetraalkylhydrazine radical cations persist for hours to days at millimolar concentrations, previous attempts at isolation of $\mathbf{1}^{+\cdot}$ salts, even in the cold, have led only to their decomposition. The cation radical lifetimes are distinctly shorter at high concentrations.[3]



$$R_2\ddot{N}{-}\ddot{N}R_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} R_2N\overset{+\cdot}{-}NR_2 \quad E_1^0$$

1 $\quad$ $1^{+\cdot}$

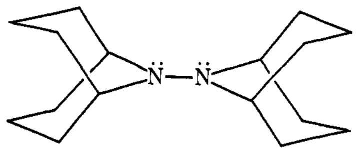
The structures of $\mathbf{1}^{+\cdot}$ are indicated by ESR studies[4] to have nearly parallel spin-bearing orbitals on nitrogen, and low activation energies for bending at nitrogen; they have a "three electron π bond".[5] Removal of the formally antibonding π electron might be expected to be relatively facile, and a second, irreversible oxidation wave with a peak potential above +1 V vs. SCE was observed for several examples of **1**, and attributed to removal of the second electron.[5] The dication $\mathbf{1}^{2+}$, with its adjacent positive charges, would be expected to deprotonate or react with nucleophiles very rapidly, so it is not surprising that the dication lifetime is short, making the second oxidation wave irreversible. We hypothesized that the reason for our failure to be able to concentrate $\mathbf{1}^{+\cdot}$ solutions without destruction of the radical cation is that $\mathbf{1}^{+\cdot}$ disproportionates to give the extremely reactive dication and basic hydrazine, leading to decomposition in spite of the low disproportionation constant.



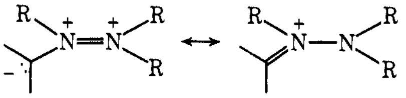
$$R_2N\overset{+\cdot}{-}NR_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} R_2\overset{+}{N}{=}\overset{+}{N}R_2 \quad E_2^0$$

$1^{+\cdot}$ $\quad$ 1^{2+}

The bis-bicyclic tetralkylhydrazine **2**[6] was prepared by photolytic nitrogen expulsion from the tetrazene[7] obtained by iodine oxidation[8] of 9-amino-9-azabicyclo[3.3.1]nonane.[9] The cyclic voltammogram of **2** shows two completely reversible one electron oxidation waves, $E_1^0 = -0.01$, $E_2^0 = +1.18$ V vs. SCE, in acetonitrile at room temperature, even at 20 mV/s scan rates. The lifetime of $\mathbf{2}^{2+}$, even in the presence of the basic hydrazine, therefore exceeds several seconds. The geometrically imposed requirement that the α-CH bonds be perpendicular to the charge-bearing orbitals on nitrogen clearly has a huge effect on the rate of deprotonation, as anticipated on the basis that the deprotonated form is precluded from having iminonium ion resonance stabilization as indicated in **3b**, a Bredt's rule effect. Because disproportionation of $\mathbf{2}^{+\cdot}$ would not lead to its immediate destruction, we attempted isolation of this cation. Oxidation of **2** with nitrosonium hexafluorophosphate[10] in methylene chloride gave gas evolution, and solvent removal gave crude $\mathbf{2}^{+\cdot}\ PF_6^-$, which was recrystallized from methylene chloride-chloroform or ethanol to give light yellow air stable flakes, 283–286 °C dec.[11] The ESR spectrum of this solid (powdered, 10^{-4} *m* in KBr) consisted of a single broad line, 5.3 G peak-to-peak, and Faraday balance measurements give $\mu_{eff} = 1.82$ (at 5.92×10^3 G), close to the value of $3^{1/2}$ predicted for a doublet species with orbital moments quenched. Solutions are yellow (λ_{max} 345 nm, log ε 3.56 in 95% ethanol) and give the same intensity ESR spectrum as does electrochemical or chemical oxidation of **2** at the same concentration. The ESR spectrum consists of five broad lines in 1:2:3:2:1 ratio, $a(2N) = 13.15$ G, with a fine structure of many lines separated by about 0.2 G partially resolvable with difficulty.



2



3a **3b**

The systems most comparable to $\mathbf{2}^{+\cdot}$ and $\mathbf{2}^{2+}$ in having one or two positive charges formally localized on adjacent heteroatoms are the mono- and dications of the eight-membered ring cyclic disulfide **4** reported by Musker, Wolford, and