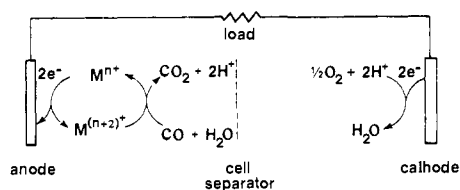


Scheme I. Generalized CO/O₂ Fuel Cell Employing the Two-Electron Redox Couple M^{(n+2)/n+} of a Homogeneous Electrocatalyst^a



^a The maximum open circuit potential, V_{oc} , of such a cell is given by $V_{oc} = |E_{1/2}(M^{(n+2)+}/M^{n+}) - E_{1/2}(O_2/H_2O)|$.

results comprise a sufficient set of preconditions for the electrocatalytic oxidation of CO at potentials approaching +0.40 V vs. SCE. Results of steady-state i - V behavior of the electrochemical oxidation of CO in the presence and absence of $[Rh^I(CO)_2Br_2]^-$ at 25 °C are presented in Figure 1. The background current at a GCE in 0.1 M HBr under an Ar atmosphere (---) is shown at the bottom of the figure. When this same solution is saturated with CO (—), no discernible increase over background current is observed. We note that at these conditions the expected reversible potential for CO oxidation, $E^\circ(CO_2/CO)$, is ~ -0.40 V vs. SCE. This result suggests that CO is not oxidizable at a GCE in 0.1 M HBr at potentials 1.20 V more anodic than expected from thermodynamic considerations alone. When $[Rh^I(CO)_2Br_2]^-$ is added to 0.1 M HBr solutions under Ar, the oxidation of Rh^I to Rh^{III} is evidenced, beginning at $V \sim +0.40$ V vs. SCE (---). When solutions of $[Rh^I(CO)_2Br_2]^-$ are placed under a CO atmosphere, a significant increase of ~ 12 mA/cm² in anodic current densities associated with the oxidation of Rh^I is observed (—). This result suggests that in the presence of CO, Rh^{III} generated at the surface of a GCE can be reduced by CO and reoxidized at the electrode on a time scale that is faster than mass transport of Rh^I from the bulk solution. The complex $[Rh^I(CO)_2Br_2]^-$ is thus functioning as an electrocatalyst, mediating the oxidation of CO at potentials where no oxidation can be seen in its absence.

Rotating disk electrode (RDE) techniques¹⁸ were used to determine the activation parameters for electrocatalytic oxidation of $[Rh^I(CO)_2Br_2]^-$. At 25 °C the heterogeneous rate constant for the oxidation of $[Rh^I(CO)_2Br_2]^-$ at glassy carbon is $k^h = 1.86 \times 10^2$ cm s⁻¹ in 0.1 M HBr.¹⁹ The dependence of this rate constant on temperature has been examined over the range 25–55 °C, from which we find: $\Delta H^\ddagger = 4.87$ kJ mol⁻¹ and $\Delta S^\ddagger = -16.8$ J mol⁻¹ K⁻¹. The negative activation energy is consistent with the formation of a restricted activated complex at the electrode surface during oxidation. The small enthalpic term and negative entropic term underscore the advantage of electrocatalysts that can function at relatively low temperatures.

The electrocatalytic oxidation of CO by $[Rh^I(CO)_2Br_2]^-$ can be incorporated into laboratory-scale fuel cells of the general type shown in Scheme I. In these cells, the $2e^-$ CO/H₂O reducing equivalent is used to effect reduction of the oxidized form of the catalyst, $M^{(n+2)+}$, to M^{n+} , with concomitant CO₂ formation. In a separate step, the reduced form, M^{n+} , is oxidized at an electrode, regenerating $M^{(n+2)+}$. The electrons released at the electrode are then available to sustain an electrical load and complete the cathodic process: reduction of O₂ to H₂O. The net chemical reaction is that of eq 1. We have examined the output characteristics of fuel cells designed as follows. A graphite anode is immersed in 40 mL of a 2.0 mM solution of $[Rh^I(CO)_2Br_2]^-$ in 0.1 M HBr. The anode compartment is charged with 1 atm of CO and connected to a GC gas-sampling loop. A Nafion 117 membrane separates the two cell compartments. The cathode compartment consists of a Pt gauze immersed in 0.1 M HBr solution through which a steady stream of air is bubbled. In a cell kept at 80 °C for 72 h, 1.21 mmol of CO₂ was observed by

GC to have been produced while 2.71 mmol of electrons were passed through the cell. This corresponds to an average current efficiency of 90% for the conversion of CO and O₂ to CO₂ and electricity. During this time the $[Rh^I(CO)_2Br_2]^-$ electrocatalyst completed 15.1 cycles. The typical open circuit potential for this cell was ~ 0.40 V. At the end of this run, $[AsPh_4]Cl$ was added to the anode compartment and $[Rh^I(CO)_2Br_2]^-$ was recovered quantitatively as a pale yellow solid, as confirmed by its characteristic IR spectrum.²⁰

We have thus shown that $[Rh(CO)_2Br_2]^-$ is an electrocatalyst for the oxidation of CO to CO₂ and that fuel cells based on homogeneous electrocatalysts can be constructed. Homogeneous electrocatalysts offer the ability to function efficiently at relatively low temperatures and may find significant applications in fuel cell research.

Acknowledgment. This research was supported in part by the DOE through a grant administered by the Energy Policy Research and Information Program at Purdue University. We also thank Conoco, Inc., and Nalco Chemical Co. for grants administered by the Coal Research Center at Purdue for their support of this research. We are particularly indebted to Dr. Thomas E. Cole for many stimulating discussions, suggestions, and experimental assistance. The loan of a potentiostat and coulometers from Bioanalytical Systems, Inc., and a generous gift of Nafion film from E.I. duPont de Nemours & Co., Inc., are also gratefully acknowledged.

Registry No. CO, 630-08-0; $[Rh(CO)_2Br_2]^-$, 44516-32-7.

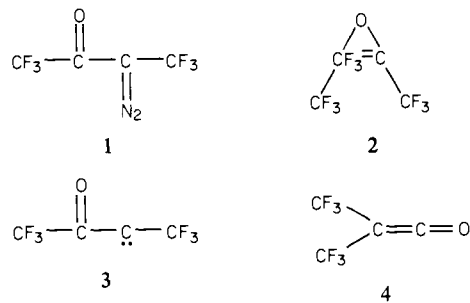
Photochemistry of Perfluoro-3-diazo-2-butanone¹

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Stimulated by the hope of preparing the first observable oxirene,^{3,4} we undertook several years ago an infrared study of the photolysis in matrix isolation of the title compound (1).⁵ Our



quest brought to light some interesting photochemistry but failed to yield detectable amounts of either perfluorodimethyloxirene (2) or a ketocarbene (3) intermediate. We were thus surprised by the recent report of Strausz et al.⁶ that matrix photolysis of

(1) This report is based principally on the Ph.D. Dissertation of E.D.L. (Laganis, E. D. Ph. D. Dissertation, Dartmouth College, Hanover, NH, 1979).

(2) Present address: Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898.

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(19) k^h is obtained at $E_p = 0.66$ V vs. SCE. RDE area: 0.0491 cm².

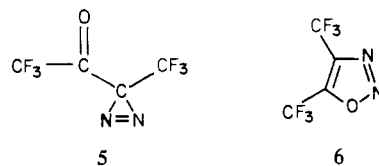
(20) IR (Nujol) $\nu(CO)$ 2060 (vs), 1980 (vs) cm⁻¹. See ref 11 and 14.

1 produces both species, as revealed by their infrared spectra. An earlier paper from the Canadian group⁷ had reported ESR detection of a triplet ketocarbene formed by matrix photolysis of **1**, but no one had ever observed a ketocarbene by IR spectroscopy.

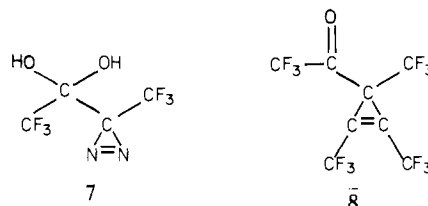
Diazo ketone **1** shows ultraviolet maxima in cyclohexane at 235 (13 300), 263 (4740), and 357 nm (36). We irradiated it using a high-pressure mercury arc with and without cutoff filters in argon matrices at ~10 K, with infrared monitoring.⁸ Perfluorodimethylketene (**4**), the product of Wolff rearrangement,⁹ was formed at all wavelengths. An unknown species having an IR band at 1761 cm⁻¹ was also observed when a 320-nm cutoff filter was used but not when a Pyrex filter (280-nm cutoff) was in place. Structures **2** and **3** were considered attractive candidates for the unknown until it was found that *brief irradiation at shorter wavelengths (>280 nm) transformed it not only into the ketene **4** but also in part to **1**, thus suggesting that the new compound contained nitrogen.*

We then discovered that this compound can be prepared at room temperature, where it is stable. Irradiation at >320 nm in isopentane/methylcyclohexane (5:1) gave the unknown together with products formed by attack on the solvent, whether the reaction was run at room temperature or 77 K. The contamination problem was not solved by working in the gas phase, for long-wavelength irradiation of **1** in a Pyrex bulb gave ketene **4** and its isomer perfluoromethacrylyl fluoride,¹⁰ among others, but none of the desired compound. Though attack on solvent occurred again in carbon tetrachloride, here the unknown represented 40–45% of the area in the ¹⁹F NMR spectrum of the products.

Trapping from a gas chromatograph gave this compound as a highly volatile, colorless liquid.¹¹ IR (Ar matrix, 15 K) 1761(m), 1745(w), 1669(w), 1361(w), 1337(w), 1289(m), 1233(m), 1224(m), 1206(s), 1196(s), 1166(m), 1133(w), 1104(m), 1047(w), 1033(w), 1013(m), 906(w), 864(m), 835(w), 747(w), 720(w), 693cm⁻¹(m). This spectrum confirmed that the stable liquid was identical with the unknown prepared earlier in matrix isolation, and the spectrum agreed excellently with that assigned by Strausz et al. to ketocarbene **3**.⁶ Though we found several additional bands, all 12 bands above 600 cm⁻¹ reported by his group closely matched counterparts in our spectrum.¹² The ¹⁹F spectrum (5:1 isopentane/methylcyclohexane) comprised two binomial quartets of equal area at δ 65.91 and 76.24, $J = 4.0$ Hz;¹³ MS, m/e 206 (parent). These data were interpretable in terms of two isomers of the starting diazoketone, diazirine **5** or oxadiazole **6**. Photoisomerization of diazo ketones to diazirines is precedented,^{14,15}



but photoisomerization to oxadiazoles is not. In fact, no simple 1,2,3-oxadiazole has ever been synthesized.¹⁶ Nonetheless, in view of the notable ability of perfluoroalkyl groups to stabilize labile structures,¹⁷ additional evidence was needed in order to distinguish unequivocally between **5** and **6**. The new compound reacted immediately with water to form a hydrate (**7**) (showing



no H–F spin coupling), a transformation that could be reversed by addition of phosphorus pentoxide. These observations, typical for highly fluorinated ketones,¹⁸ confirm the assignment of structure **5** to the volatile unknown. Ketones **5** and **8**¹⁹ display essentially identical carbonyl stretching frequencies.²⁰

Perfluoro-3-acetyl-3-methyldiazirine (**5**) decomposed at 75–80 °C in carbon tetrachloride to yield the solvent-containing products observed in the photolysis of **1**.¹¹ Heated in the vapor phase at 80 °C for 3.5 h in an atmosphere of argon (300 mm), **5** underwent clean and complete fragmentation–rearrangement to ketene **4**. Since diazoketone **1** is stable to much higher temperatures, the diazirine must lose nitrogen directly, not via its open-chain isomer.²¹ As noted above, the same overall transformation takes place photochemically but in this case at least partly via **1**.^{22,23}

We are not able to evaluate Strausz's claim to have prepared the first oxirene by photolysis of **1**,⁶ for we did not observe the infrared spectrum he reported for the compound under any of our photolysis conditions. While we irradiated with the full mercury arc and in wavelength regions >280 nm, we did not photolyze **1** specifically at 270 nm, the wavelength at which the presumed oxirene was formed. By examining the photolysis of homologues of **1**, the Canadian researchers have found strong evidence that the species in question is symmetrical. The absence of infrared absorption above 1325 cm⁻¹ is certainly unexpected for an oxirene, however. Whatever it may be, Strausz' very labile entity promises to be novel.

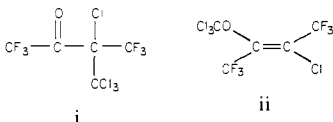
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(8) In hydrocarbon solvent at ambient temperatures diazo ketone **1** exists as a ~7:3 mixture of the *E* and *Z* isomers, respectively. The ratio (before irradiation) in our argon matrices was presumably similar given the very rapid cooling during matrix deposition.

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(11) The other major product, which gave rise to a GC peak at much longer retention time, was a liquid with these spectral properties: MS, m/e 295 (contains 3 Cl); IR 1861, 1777 cm⁻¹; ¹⁹F NMR δ 63.00 (q, $J = 1.2$ Hz), 63.79 (q, $J = 1.2$), 64.96 (q, $J = 2.2$), 70.42 (q, $J = 2.2$). If the highest m/e peak is ($M^+ - Cl$), this product has the composition of a ketocarbene 3/carbon tetrachloride adduct. The IR and NMR spectra are consistent with a roughly equimolar mixture of adducts i and ii.



(12) In light of the high selectivity and sensitivity of ESR relative IR, failure to observe the ketocarbene by the latter technique is not surprising.

(13) Chemical shifts are reported in ppm upfield from internal trichlorofluoromethane.

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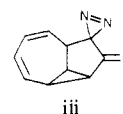
(15) Analogous photorearrangement has been found with diazo amides: (a) Voigt, E.; Meier, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 103; *Chem. Ber.* **1975**, *108*, 3326. (b) Franich, R. A.; Lowe, G.; Parker, J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2034. Lowe, G.; Parker, J. *J. Chem. Soc. D.* **1971**, 1135.

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(19) At room temperature **5** has $\nu_{C=O} = 1769$ cm⁻¹ (vapor); cf. **8**, $\nu = 1770$ cm⁻¹ (film). Boriack, C. J.; Laganis, E. D.; Lemal, D. M. *Tetrahedron Lett.* **1978**, 1015.

(20) The weak N=N stretching bond in diazirines is frequently not reported. $\nu_{N=N}$ for **5** at 1669 cm⁻¹ may be compared with that for ketodiazirine iii at 1630 cm⁻¹ (KBr).^{14a}



(21) Some diazirines bearing carbonyl groups at the 3-position rearrange to their diazo isomers on standing or heating.^{14b,15a} (22) The photoisomerization of certain diazo amides^{15b} and a diazo ketone^{14a} to the corresponding diazirines has been found to be photoreversible. (23) For a review of diazirine thermolysis and photolysis, see: Liu, M. T. H. *Chem. Soc. Rev.* **1982**, *11*, 127.

Acknowledgment. We are grateful for generous financial support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Note Added in Proof. Professor Strausz has kindly informed us that, subsequent to the appearance of his recent paper,⁶ he found strong evidence against the ketocarbene assignment for the carbonyl-containing species observed by IR. In particular, matrix photolysis of perfluoro-4-diazo-3-pentanone gave concentrations of the derived ketocarbene which were too low to detect by ESR, yet IR revealed a carbonyl-bearing species analogous to that from **1**. The Strausz group has made an additional interesting observation, viz. that vapor-phase photolysis of **1** in the presence of perfluoro-2-butyne at $\lambda \geq 320$ nm yields a ketocarbene trapping product, perfluorotetramethylfuran.

Registry No. **1**, 2834-21-1; **5**, 87282-23-3; **7**, 87282-24-4.

Isolation and X-ray Structure of $[\text{Li}_2(\mu_3\text{-}t\text{-Bu}_2\text{P})(\mu_2\text{-}t\text{-Bu}_2\text{P})(\text{C}_4\text{H}_8\text{O})]_2$ Containing a Staggered, Planar Li_4 Unit. The First Structurally Characterized Alkali Metal Diorganophosphide

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Alkali metal diorganophosphides (MPR_2 , M = Li, Na, K, ...; R = alkyl, aryl) have been used for many years as useful synthetic reagents in both organic and inorganic chemistry.¹ Although they are normally represented simply as " MPR_2 ", very little is known about their actual constitution in solution or in the solid state. In solution molecular weight measurements have suggested some degree of aggregation,² and recent NMR studies by McFarlane and co-workers suggested a dimeric structure for LiPPh_2 in diethyl ether.³

Structural information on lithium derivatives is available for a number of alkyls,⁴ aryls,⁵ dialkylamides,⁶ and alkoxides.⁷ We report here the isolation and X-ray crystal structure of $[\text{Li}_2(\mu_3\text{-}t\text{-Bu}_2\text{P})(\mu_2\text{-}t\text{-Bu}_2\text{P})(\text{C}_4\text{H}_8\text{O})]_2$ (**1**), which to our knowledge is the first structurally characterized alkali metal diorganophosphide to be reported.

As part of a study of the steric effects of bulky phosphide (R_2P^-) groups as ligands for d-block transition metals, we have used the

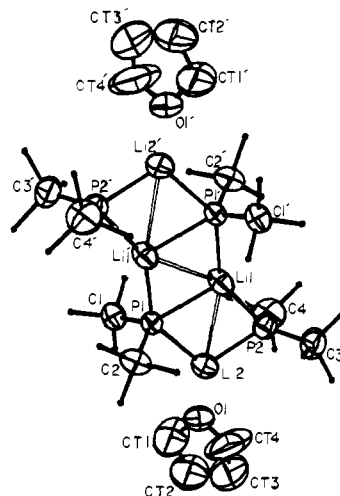


Figure 1. General view of $[\text{Li}_2(\mu_3\text{-}t\text{-Bu}_2\text{P})(\mu_2\text{-}t\text{-Bu}_2\text{P})(\text{C}_4\text{H}_8\text{O})]_2$ (**1**). For clarity methyl groups of the *t*-Bu units are represented as sticks.

lithium derivative of di-*tert*-butylphosphine " $\text{Li}^i\text{Bu}_2\text{P}$ " generated in situ.⁸ In order to correlate factors such as the reactivity, the degree of aggregation, and the steric bulk of the alkyl groups, we have isolated and characterized crystals of this useful starting material.

Evaporation to dryness of pale yellow " $\text{Li-}t\text{-Bu}_2\text{P}$ " solutions, generated in situ in Et_2O or THF, followed by recrystallization of the residue from hexane at -20 °C yields large colorless crystals of **1** in high yield. These crystals rapidly crumble to a white powder under vacuum or in the absence of either hexane or THF vapor. Crystals suitable for X-ray diffraction were therefore mounted in thin-walled glass capillaries under a nitrogen atmosphere saturated with hexane vapor.

A view of the molecular structure of **1** is shown in Figure 1.⁹ There are a number of interesting features. The structure consists of an unusual distorted "Z" of four Li atoms, all of which have virtually planar coordination geometries. The Li-Li distances of 3.065 (13) Å (Li(1)-Li(2)) and 3.025 (19) Å (Li(1)-Li(1')) suggest that direct Li-Li bonding is relatively unimportant.⁴ There is a crystallographically imposed center of inversion at the midpoint of the two central Li atoms (Li(1) and Li(1')). Two of the phosphide groups (P(1) and P(1')) are triply bridging to three Li atoms while the other two (P(2) and P(2')) bridge only two (see Figure 1). The two end Li atoms (Li(2) and Li(2')) each bear a coordinated THF molecule. The overall Li_4P_4 framework is virtually planar.¹⁰ The Li-P distances for the doubly bridging P atoms (P(2) and P(2')) are notably shorter by ca. 0.15 Å than those of the triply bridging phosphorus atoms.¹¹ These distances

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(9) Mp 113-115 °C; IR (Nujol mull, KBr plates) 1258 (m), 1160 (m), 1100 (m), 1028 (m), 795 (m), 665 (m) cm^{-1} ; ^1H NMR (in C_6D_6) at 31 °C, δ 3.69 (m, 8 H THF), 1.67 (s, ($\Delta\omega_{1/2} = 6$ Hz), 36 H, Bu), relative to Me_4Si δ 0.0. The other THF peak is obscured by the *t*-Bu resonance. CAD 4, crystal data: $\text{Li}_2\text{O}_2\text{P}_4\text{C}_{40}\text{H}_{88}$, monoclinic, space group $\text{P}2_1/n$, $a = 11.816$ (1) Å, $b = 20.490$ (2) Å, $c = 12.356$ (5) Å, $\beta = 96.95$ (2)°, $U = 2969.6$ (3) Å³, $D_c = 0.842$ g cm^{-3} , $Z = 2$ (tetramers), $\lambda(\text{Mo K}\alpha) = 0.71069$ Å (graphite monochromator), $\mu(\text{Mo K}\alpha) = 1.5$ cm^{-1} . Patterson and difference Fourier techniques were used to solve and refine the structure. Refinement (full matrix, least squares) of 2162 reflections ($I > 2\sigma(I)$), 5562 measured ($4^\circ < 2\theta < 50^\circ$), gives current R and R_w values of 0.0982 and 0.1312, respectively. Data/parameter ratio = 9:1. All non-hydrogen atoms anisotropic, hydrogen atoms not located. We think that the relatively high R values are due to substantial thermal motion, especially in the THF molecules. We plan to collect a low-temperature data set in order to try to resolve this. Details will be published separately.

(10) Deviations (in Å) from the best least-squares planes are as follows. Plane 1 (Li(1)-Li(2)-P(1)-P(2)): Li(1) -0.033 (17), Li(2) 0.034 (19), P(1) 0.032 (3), P(2) 0.035 (3). Plane 2 (Li(1)-Li(1')-P(1)-P(1')): Li(1) 0.006 (17), Li(1') 0.006 (14), P(1) -0.006 (3), P(1') 0.006 (2). Dihedral angle between planes 1 and 2 = 2.5 (2) Å.

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