(Me)CH–MLn and $R_fCH_2CH_2$–MLn (L = CO and $R_fCH{=}CH_2$). A possible mechanism that can accommodate the unique results is depicted in Scheme I.

As trifluoromethyl and pentafluorophenyl groups (abbreviated as R_f) are strongly electron-withdrawing substituents, a negative charge on the α-carbon stabilizes α-(R_f)ethylmetal species, intermediate [A], while a positive charge on the α-carbon destabilizes intermediate [A]. Thus, if the MLn moiety induces a negative charge on the α-carbon, the branched intermediate [A] should be stabilized, and then the formation of isoaldehyde should be predominant: as a matter of course, if the MLn moiety induces a positive charge on the α-carbon, the unbranched intermediate [B] should be preferable, which leads to the formation of *n*-aldehyde. It is strongly suggested that the relative stability of the branched alkylmetal intermediate [A] increases in order R_f(Me)CH–CoLn < R_f(Me)CH–PtLn < R_f(Me)CH–RuLn < R_f(Me)CH–RhLn, i.e., the cobalt species may cause a fairly large positive charge on the α-carbon whereas the rhodium species may generate relatively large negative charge on the α-carbon, and the platinum and ruthenium species can be placed between cobalt and rhodium, in the present systems. However, a detailed understanding of the mechanisms of the present reactions should await further investigation.

Registry No. TFP, 677-21-4; PFS, 653-34-9; $Co_2(CO)_8$, 10210-68-1; $PtCl_2$(DIOP), 65582-87-8; $Ru_3(CO)_{12}$, 15243-33-1; $Rh_6(CO)_{16}$, 28407-51-4; Rh, 7440-16-6; $HRh(CO)(PPh_3)_3$, 17185-29-4; RhCl(dppb), 81725-30-6; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(CO)(PPh_3)_2$, 13938-94-8; $RhCl_3{\cdot}3H_2O$, 13876-89-6.

Solvent-Dependent Reactions of Carbon Dioxide with a Platinum(II) Dihydride. Reversible Formation of a Platinum(II) Formatohydride and a Cationic Platinum(II) Dimer, $[Pt_2H_3(PEt_3)_4][HCO_2]$

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Reactions of carbon dioxide with transition-metal compounds are relevant to CO_2 activation and catalysis of the water–gas shift reaction.[1] The properties of formate ion as a ligand have also attracted attention,[1-4] and metal-catalyzed decomposition of formate ion to yield CO_2 and metal hydride (reaction 1) has been

$$M^+ + HCO_2^- \rightleftharpoons M{-}O_2CH \rightleftharpoons M{-}H + CO_2 \qquad (1)$$

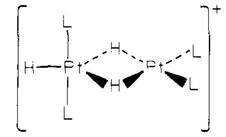
suggested as a key step in several systems that homogeneously catalyze the water–gas shift reaction.[3,5] We describe herein the unusual solvent dependence of the reactions of carbon dioxide with a sterically unhindered platinum(II) dihydride, a system that catalyzes the transformation of formic acid to carbon dioxide and hydrogen, and a mechanism for catalysis.

A toluene solution of predominantly *trans*-dihydrobis(triethylphosphine)platinum(II)[6] (**1**) under one atmosphere of carbon dioxide consists of an equilibrium mixture of **1** and *trans*-(formato)hydrobis(triethylphosphine)platinum(II) (**2**) (reaction 2).

$$\underset{\mathbf{1}}{PtH_2L_2} + CO_2 \overset{K}{\rightleftharpoons} \underset{\mathbf{2}}{trans\text{-}PtH(O_2CH)L_2} \qquad (2)$$

A signal for **2** appears in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.8 (s, $^1J_{Pt-P}$ = 2843 Hz). Examination of the ^1H NMR spectrum of this solution reveals a signal for formate hydrogen [H_a: δ 9.36 (d, br, $^4J_{H_a-H_b}$ = 4 Hz, $^3J_{Pt-H_a}$ = 47 Hz)] and a signal for hydride [H_b: δ −21.26 (td, $^2J_{P-H_b}$ = 16 Hz, $^4J_{H_b-H_a}$ = 4 Hz, $^1J_{Pt-H_b}$ = 1176 Hz)]. The presence of ^{195}Pt satellites for the formate hydrogen signal establishes that formate ion binds to platinum.[7] From the integrated intensities of the $^{31}P\{^1H\}$ NMR spectra, the equilibrium constant is approximately 2 atm^{-1} at 25 °C.

In polar solvents such as acetone or acetonitrile, **1** reacts rapidly with 1 atm of CO_2 at 25 °C to form a cationic platinum dimer, $[Pt_2H_3L_4]^+$ (**3**, L = PEt_3), and free formate ion. Addition of $LiBF_4$ yields a precipitate of $LiHCO_2$. Metathesis of **3a** with $NaBPh_4$ produces $[Pt_2H_3L_4][BPh_4]$ (**3b**), isolable as a yellow, crystalline, air-stable solid.[8] Analysis of the ^1H, ^{31}P, and ^{195}Pt NMR spectra of solutions of **3a** and **3b** reveals that the cation contains two inequivalent platinum centers, each bound to a pair of mutually equivalent triethylphosphine ligands. The metal centers are bridged by a pair of equivalent hydride ligands, and a third hydride ligand binds to one platinum, which is 5-coordinate.[9] These facts are consistent with the structure (**3**), and an analogous structure has been proposed for the cation $[Pt_2H_3(PPh_3)_4]^+$.[10]



3a = $[Pt_2H_3L_4][HCO_2]$
3b = $[Pt_2H_3L_4][BPh_4]$
L = PEt_3

Solvent strongly influences the reactions of carbon dioxide with **1**. Formation of **3a** in polar solvents may occur because these media stabilize charge-separated species; this solvent influence is primarily of *thermodynamic* origin. Support for this view comes from the observation that **3a** reverts to neutral monomers when extracted into toluene. Coordinating solvents could also exert a *kinetic* effect by displacing formate ion[11] from **2** to yield the solvated (S = solvent) cation $PtH(S)L_2^+$ (**4**), which could then react with **1** to form **3**.

That **3a** forms reversibly from **1** and CO_2 is indicated by the following experiments. Bubbling hydrogen through a solution of **3a** (at 25 °C) sweeps CO_2 from the system and regenerates **1**.

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(6) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–1140. In hydrocarbon solvents **1** exists as predominantly the trans isomer; however, it is in equilibrium with the cis form. In polar solvents significant (10%) quantities of the cis isomer are present at equilibrium.

(7) The complex *trans*-$PtH(O_2CH)[P(c\text{-}Hx)_3]_2$ has been shown by X-ray diffraction to be a monodentate O-bonded formato complex (ref 5). The close correspondence of the ^1H NMR parameters of this complex and those of **2** suggest an analogous structure for **2**.

(8) Anal.: % found (% calcd) C, 48.90 (48.65); H, 7.01 (7.06); P, 10.48 (10.45); Pt, 32.68 (32.92); B (by difference), 0.91 (0.93).

(9) $[HPt^A(P^AEt_3)_2(\mu\text{-}H)_2Pt^B(P^BEt_3)_2][BPh_4]$ (acetone-d_6, 30 °C): $^{31}P\{^1H\}$ NMR δ P^A 20.8 (t, $^1J(Pt^AP^A)$ = 2741, $^2J(Pt^BP^A)$ = 23 Hz), δ P^B 24.2 (t, $^1J(Pt^BP^B)$ = 2540, $^2J(Pt^AP^B)$ = 23, $^3J(P^AP^B)$ = 2.9 Hz); $^{195}Pt\{^1H\}$ NMR δ Pt^A −708, Pt^B −358 ($^1J(Pt^APt^B)$ = 866 Hz); ^1H NMR H^{term} δ −4.91 (m, $^1J(Pt^AH)$ = 1316, $^2J(Pt^BH)$ = 191 Hz), H^{bridg} δ −3.55 (m, $^1J(PtH)$ = 361, $^1J(Pt'H)$ = 592 Hz).

(10) Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155–156.

(11) Weakly coordinating solvents can displace oxygen donor anions such as OCH_3^- and OH^- that bind trans to a ligand (H, alkyl, PR_3) of high trans influence: (a) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993–999. (b) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–2038. (c) Reference 3a. (d) Arnold D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119–135. Roundhill, D. M. *Adv. Organomet. Chem.* **1975**, *13*, 274–361.

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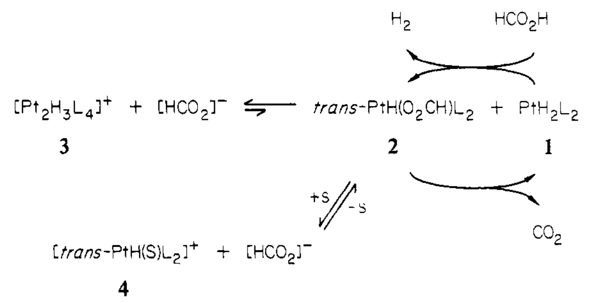
Scheme I. Proposed Equilibria in the Catalysis of $HCO_2H \rightarrow H_2 + CO_2$ ($L = PEt_3$; $S = HCO_2H$, $(CH_3)_2CO$, or CH_3OH)



In solution under 1 atm of ethylene, **3a** quantitatively converts to $Pt(C_2H_4)L_2$ after 24 h (reaction 3). We have shown[6] that

$$\underset{\mathbf{3}}{[Pt_2H_3L_4]^+} + [HCO_2^-] \underset{CH_3CN}{\rightleftharpoons} \underset{\mathbf{1}}{PtH_2L_2} + \textit{trans}\text{-}PtH(O_2CH)L_2 \xrightarrow[-CO_2]{C_2H_4} 2Pt(C_2H_4)L_2 + 2H_2 + CO_2 \quad (3)$$

ethylene reacts rapidly with **1** to yield $Pt(C_2H_4)L_2$ and H_2. This apparently drives reaction 3. It is important to note that under identical conditions, **3b**, in the absence of HCO_2^-, did not react with ethylene. Solutions of **3a** placed under 1 atm of $^{13}CO_2$ also rapidly incorporate ^{13}C into the formate counterion. Dimer **3a** therefore appears to react via the small equilibrium concentrations of PtH_2L_2 and $PtH(O_2CH)L_2$.

The complex *trans*-$PtH(O_2CH)[P(i\text{-}Pr)_3]_2$ catalyzes the decomposition of formic acid to hydrogen and carbon dioxide,[3a] a reaction relevant to water-gas shift catalysis.[3,4] The complex $PtCl_2[P(n\text{-}C_4H_9)_3]_2$ has been reported[12] to slowly catalyze formic acid decomposition at high temperatures. Solutions of **3b** show no such catalytic activity after 14 h at 20 °C.[13] However, when sodium formate was added ($[HCO_2^-]:[\mathbf{3}] = 200$), immediate sustained catalysis occurs at a turnover rate of 3.3 ± 0.5 (mol HCO_2H/mol **3**) per hour *at 20 °C*. This rate decreases as the pressure of CO_2 and H_2 above the solution increases, but when these gases are removed, the original catalytic rate returns. Several hundred turnovers were observed with no significant change in activity. A mechanism based on the equilibria described above is diagrammed in Scheme I. Catalytically active platinum species are proposed to be the monomers **1** and **2** present in equilibrium with dimer **3a**. Formate ion promotes catalysis by its reaction with **3** to produce small steady state quantities of **1** and **2**. We independently established that **1** reacts rapidly with formic acid to evolve hydrogen and produce formate ion.[14] Because **2** and **4** should also be in equilibrium in coordinating solvents, excess formate ion should further promote the catalysis by driving this equilibrium toward **2**. Loss of carbon dioxide from **2** completes the cycle. The catalytic cycle can in fact be entered by adding an excess of sodium formate to **4** (as [*trans*-$PtH((CH_3)_2CO)L_2][BF_4]$). Note that the proposed catalytic species **1** and **2** were not detectable by $^{31}P\{^1H\}$ NMR spectroscopy of these solutions, and their concentrations relative to **3** must be quite small. This implies that the turnover rate per molecule of **1** or **2** must be much greater than the turnover rate calculated on the basis of added platinum.[15] The dimerization reaction thus traps and inactivates the catalytic species.[16]

Acknowledgment. We thank the National Science Foundation (Grants CHE 78-01615 and 81-050698) for support of the work and Johnson Matthey, Inc., for a generous loan of platinum.

Registry No. 1, 62945-61-3; **2**, 81768-78-7; **3a**, 81800-04-6; **3b**, 81800-05-7; CO_2, 124-38-9; HCO_2H, 64-18-6.

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(12) Coffey, R. S. *Chem. Commun.* **1967**, 923-924.

(13) $[\mathbf{3b}]_0 = 0.0063$ M, $[HCO_2H]_0 = 9.8$ M, methanol solvent.

(14) In this reaction, a mixture of **3** and **4** rapidly forms. We believe **1** reacts with formic acid to give **4**, either by direct protonation and loss of H_2 or by oxidative addition of HCO_2H and reductive elimination of H_2, with intermediate formation of **2**. (This accords with observations of the reactivity of **1**: ref 6.) Complex **4** (or **2**) can then react with unreacted **1** to give **3**.

(15) On the basis of our limits of detection by $^{31}P\{^1H\}$ NMR spectroscopy of 1%, the turnover rate based on **1** or **2** would be *at least* 2 orders of magnitude greater than the turnover rate based on **3** or **4**.

(16) If these monomeric species were anchored to a rigid support to prevent dimerization, a dramatic increase in catalytic activity should be observed. This possibility is being investigated.

[2 + 2] Cycloaddition Reactions of Homoazulene. A New Synthesis of the Homoheptalene Ring System

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Recent studies on homoazulene (**1**)[1] have significantly advanced


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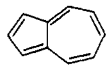
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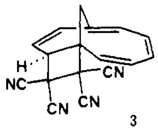
the modern view of π-torsional effects on cyclic conjugation.[2] This unusual hydrocarbon and its derivatives have also provided the first clear data on the effects of nonalternant transannular interactions in cyclic π systems; several parallels between the spectroscopic properties of **1** and those of azulene (**2**) have been noted.[3] By the synthesis developed in our laboratory,[2e,f] homoazulene has now become available in sufficient quantity to permit much more extensive physical and chemical investigation of its unique properties, and we have recently reported on the novel thermal behavior of **1**.[4] Herein we describe the first intermolecular chemical reactions of homoazulene, one of which leads to a crystalline [4*n*]annulene derivative.

At room temperature, homoazulene reacts instantaneously with tetracyanoethylene (TCNE). By conducting the reaction at −45 °C in tetrahydrofuran (0.03 M in each component) for 45 min, we obtained a 1:1 adduct in quantitative yield. Spectroscopic analysis (see Table I) permits assignment of structure **3** to this adduct; the stereoisomer of **3** with an exo tertiary hydrogen is geometrically infeasible.



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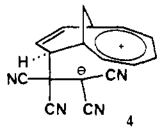

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Although symmetry forbidden as a concerted reaction, [2 + 2] cycloaddition of TCNE to alkenes frequently occurs via zwitterionic intermediates.[5] In the present case, formation of an aromatic homotropylium ion[6] very likely facilitates the electrophilic attack and accounts for the site of initial C–C bond formation (**4**). The observed periselectivity corresponds to that reported by Hafner et al. in the stepwise [2 + 2] cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to azulene,[7] and the exo stereoselectivity conforms with that observed in the electro-

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(1) Homoazulene = bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene; homoheptalene = bicyclo[5.5.1]trideca-1,3,5,7,9,11-hexaene.

(2) (a) For a discussion of the geometry of homoazulene, see: Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893. (b) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *Ibid.* **1976**, *98*, 8277. (c) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239. (d) Scott, L. T.; Brunsvold, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 4320. (e) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 274. (f) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216.

(3) Scott, L. T., unpublished results; see also ref 2c and 2f.

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