C, 45.61; H, 6.02; Cl, 6.41; mol wt, 1106. Found: C, 45.56; H, 6.13; Cl, 6.52; mol wt, 1121 (cryoscopic in benzene). For **3b**, the ^{1}H NMR (C$_6$D$_6$) exhibits singlets at δ 8.96 (30 H, line width = 6 Hz.), −154 (3 H, line width ≈ 7 Hz). Anal. Calcd for C$_{21}$H$_{33}$UCl: C, 45.12; H, 5.95; Cl, 6.34; mol wt, 559. Found: C, 44.98; H, 5.89; Cl, 6.39; mol wt, 568 (cryoscopic in benzene). (e) Anal. Calcd for C$_{40}$H$_{64}$Th$_2$ (**4a**): C, 47.61; H, 6.41; mol wt, 1009. Found: C, 48.63; H, 6.63; mol wt, 1038 (cryoscopic in benzene). (f) For **4b**, broadened bands centered at 1345 and 1180 cm^{-1} are observed in the IR. The ^{1}H NMR spectrum (C$_6$D$_6$) shows a singlet at δ −2.15 (line width = 4 Hz); the hydride signal has not, as yet, been located.

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Activation of Water Molecule. 1. Intermediates Bearing on the Water Gas Shift Reaction Catalyzed by Platinum(0) Complexes

Sir:

The heterogeneously catalyzed water gas shift reaction now employed in industry requires high temperature.[1] Homogeneous catalysts active at lower temperature are attracting considerable interest[2] because of the favorable thermodynamic equilibrium. Recently three groups have reported homogeneous catalytic systems consisting of metal carbonyls, i.e., Ru$_3$(CO)$_{12}$–base[3,4] and [Rh(CO)$_2$Cl]$_2$–HCl–NaI–glacial acetic acid.[5] The logical basis for employing metal carbonyls as catalysts might be the CO activation through coordination which facilitates nucleophilic attack by water.[3-5]

We wish to report here briefly a new approach based on a different strategy to activate the water molecule using low-valent transition metal complexes capable of forming hydrido hydroxo species, *trans*-H–M–OH. In view of HSAB principles and the strong trans influence of hydride,[6] an enhanced nucleophilic reactivity[7] toward CO is expected for the hydroxo ligand in the H–M–OH species. Possible candidates for such low-valent transition metal compounds are PtL$_3$ (L = tertiary phosphines).

The results of the water gas shift reactions catalyzed by some PtL$_3$ complexes are summarized in Table I. Typically the catalytic solution prepared from PtL$_3$ (0.1 mmol) and H$_2$O (2

Table I. The Water Gas Shift Reaction[a]

Catalyst	Solvent	Temp. °C	H$_2$	CO$_2$	Turn-over[c]
Pt[P(i-Pr)$_3$]$_3$	Acetone	100	9.4	8.2	8.8
	Acetone	125	16.0	15.8	159
	Acetone	153	37.5	31.6	345
	THF	100	7.0	6.6	68
	Pyridine	100	0.7	1.0	9
Pt(PEt$_3$)$_3$	Acetone	100	1.1	1.1	11
Pt(PPh$_3$)$_3$	THF	100	0	0	0

Gaseous Products[b]

[a] The reaction conditions shown in the text. [b] Millimoles. [c] Moles/mole of catalyst, 18 h.

mL) in an aprotic solvent (5 mL) was placed into a stainless steel bomb (100 mL) under a N$_2$ atmosphere and subsequently was charged with CO (20 atm). After heating at a fixed temperature for 18 h, the gaseous products in the vapor phase as well as dissolved in the liquid phase were analyzed by gas chromatography[3,5] and quantitative titration.

A remarkable solvent effect is observed for the catalysis. Coordinating pyridine drastically reduces the catalytic activity of Pt[P(i-Pr)$_3$]$_3$[8] (**1**). The colorless homogeneous reaction mixture in pyridine after the shift reaction (100 °C, 18 h) contains *trans*-{PtH(pyridine)[P(i-Pr)$_3$]$_2$}OH[9] (**2**) which can be stabilized by anion metathesis with BF$_4^-$ (68% yield). By contrast, from the catalytic reaction in acetone or THF carried out under the same conditions was obtained *trans*-{PtH(CO)-[P(i-Pr)$_3$]$_2$}OH (**3**) as the BPh$_4^-$ salt[10] in 90% yield.

The precursors **2** and **3** are readily traced from studies on the solution chemistry of PtL$_3$. Extensive dissociation of **1** gives PtL$_2$ as by far the predominant species in solution.[11] Consequently the oxidative addition of water occurs with PtL$_2$ to give **2** via solvation of an incipient species PtH(OH)L$_2$. The addition was found to be reversible as **1** was recovered from a mixture of **1** and H$_2$O in pyridine on concentration to dryness. The instability of **2** prevents its isolation and the rapid proton exchange between the hydrido ligand of **2** and water apparently obscures the hydrido ^{1}H NMR signal. In addition to the isolation of *trans*-{PtH(pyridine)[P(i-Pr)$_3$]$_2$}BF$_4$, the existence of **2** is further evidenced by conductometric and pH measurements. Thus the system **1**/H$_2$O in pyridine ([H$_2$O] > 15 M) shows a conductance (Λ 23.9 Ω^{-1} cm^2 at 20 °C), and the dissociation of OH$^-$ from **2** is manifested by the apparent pH (14.1) of the system **1**/H$_2$O ([**1**] = 9.8 × 10^{-3} M, [H$_2$O] = 22.2 M in pyridine, 20 °C).[12]

A reaction mixture of the water gas shift reaction (100 °C, 18 h) catalyzed by Pt(PEt$_3$)$_3$ in acetone contains a water adduct [PtH(PEt$_3$)$_3$]OH,[13] which was isolated as the BPh$_4$ salt[14] in 72% yield. In this case, the formation of [PtH(CO)-(PEt$_3$)$_2$]OH was not observed. The formation of [PtH-(PEt$_3$)$_3$]$^+$ and {PtH(pyridine)[P(i-Pr)$_3$]$_2$}$^+$ is ascribed to their inertness toward CO (1 atm, 25 °C), which accounts for the low catalytic activity of Pt(PEt$_3$)$_3$ in acetone or **1** in pyridine.

The catalytic activity of PtL$_3$ decreases in the order P(i-Pr)$_3$ > PEt$_3$ ≫ PPh$_3$. The complete lack of catalytic activity in Pt(PPh$_3$)$_3$ is apparently due to the incapability of water adduct formation. The importance of water molecule activation is obvious.

Nucleophilic attack of OH$^-$ at the coordinated CO will give PtH(CO$_2$H)L$_2$. Evidence for the metal carboxylic acid is the formation of the potassium salt *trans*-PtH(CO$_2$K)[P(i-Pr)$_3$]$_2$, observed by ^{1}H NMR and IR spectra[15] of the solution of *trans*-{PtH(CO)[P(i-Pr)$_3$]$_2$}BPh$_4$ treated with an excess of KOH in aqueous THF at room temperature. Further indirect support for the formation of the metal carboxylic acid is the successful isolation of *trans*-PtH(CO$_2$CH$_3$)[P(i-Pr)$_3$]$_2$[16] (65%

Scheme I. Possible Mechanism for the Water Gas Shift Reaction Catalyzed by Pt[P(*i*-Pr)₃]₃

L = P(i̲-Pr)₃; S=solvent
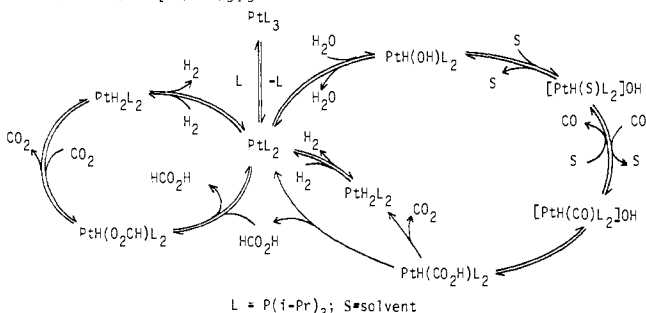
yield) by the reaction of *trans*-{PtH(CO)[P(*i*-Pr)₃]₂}BPh₄ with CH₃ONa at room temperature. Facile formation of Pt(R)-(CO₂H)(diphos) from Pt(R)(OH)(diphos) (R = CH₃, c-C₆H₉) is also known.[17]

The CO₂ evolution should occur from thermal decomposition[18] of the unstable PtH(CO₂H)L₂.[19] A dihydride species *trans*-PtH₂[P(*i*-Pr)₃]₂[20] (**4**) will then be formed. The reaction of **4** with CO leading to Pt₃(CO)₃L₄ is possible. However, this route in the catalysis is excluded since the isolated Pt₃(CO)₃[P(*i*-Pr)₃]₄[21] was found almost inactive catalytically. Thus, **4** is thought to undergo hydrogen elimination (Scheme I). Involvement of **4** in the catalytic cycle was confirmed by the dihydride-catalyzed water gas shift reaction[23] from which was isolated **3** as its BPh₄ salt.

Alternatively, reductive elimination of HCO₂H from PtH(CO₂H)L₂ with concomitant formation of Pt[P(*i*-Pr)₃]₂ is possible. A rapid catalytic decomposition of HCO₂H into CO₂ and H₂ occurs with **1** at room temperature,[24] and the platinum complex was recovered as **4** quantitatively. The decomposition of HCO₂H probably proceeds through oxidative addition of HCO₂H to give *trans*-PtH(O₂CH)[P(*i*-Pr)₃]₂, which is followed by β-hydrogen elimination affording **4** and CO₂. Consistent with this, the decomposition of HCO₂H was also catalyzed by *trans*-PtH(O₂CH)[P(*i*-Pr)₃]₂[25] prepared separately by CO₂ insertion into the Pt–H bond of **4**. The possible pathways are summarized in Scheme I.

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(10) ν(Pt–H) 2178, ν(CO) 2058 cm⁻¹; δ −4.55 (Pt–H, t, J_{P–H} = 11.3, J_{Pt–H} = 881 Hz), 1.32 (CH₃, q, ³J_{P–H} + ⁵J_{P–H} = 15.0, J_{H–H} = 7.5 Hz), ~2.7 (CH, m).
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(16) ν(Pt–H) 1985, ν(CO) 1617, ν(C–O) 1008 cm⁻¹; δ −8.98 (Pt–H, t, J_{P–H} = 17.7, J_{Pt–H} = 630 Hz), 1.17 (CH₃, q, ³J_{P–H} + ⁵J_{P–H} = 14.0, J_{H–H} = 7.0 Hz), ~2.1 (CH, m), 3.67 (CH₃O, s, J_{Pt–H} = 4.5 Hz).
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(23) The water gas shift reaction catalyzed by **4** under the same conditions (in acetone, 100 °C) shown in the text produced 46 mol of H₂ and 40 mol of CO₂/mol of catalyst.
(24) Employing Pt[P(*i*-Pr)₃]₃ (0.1 mmol) in a mixture of acetone (15 mL) and H₂O (1 mL), HCO₂H (5 mmol) decomposed at 20 °C with a half-time of 15 min.
(25) ν(Pt–H) 2200, ν(OCO) 1530, 1310 cm⁻¹; δ −21.8 (Pt–H, t, J_{P–H} = 14.8, J_{Pt–H} = 1012 Hz), 1.33 (CH₃, q, ³J_{P–H} + ⁵J_{P–H} = 14.0, J_{H–H} = 6.8 Hz), ~2.4 (CH, m), 9.5 (O₂CH, br). The platinum(II) hydrido formate complex has a precedent, *trans*-PtH(O₂CH)[P(c-C₆H₁₁)₃]₂: A. Immirzi and A. Musco, *Inorg. Chim. Acta*, **22**, L35–L36 (1977).

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Complete Kinetic Analysis of Thermal Stereomutations of (+)-(1*S*,2*S*,3*S*)-*r*-1-Cyano-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane

Sir:

Both one-center (k_i) and two-center (k_{ij}) thermal epimerizations of cyclopropanes are known in special cases,[1-3] but there is no reliable method for anticipating the relative importance of these reaction modes in other cyclopropyl systems. Only experiments capable of discriminating among all one-center and all two-center epimerization possibilities can provide the factual grounds for developing theory appropriate to this task.

To synthesize the substrate selected for our kinetic studies, (+)-(1*S*,2*S*,3*S*)-*r*-1-cyano-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane ((+)-**1**-*c*), *trans*-β-deuteriostyrene,[4] and ethyl diazoacetate-*d*₁[5] were reacted in the presence of CuSO₄; the resultant mixture of esters was epimerized with potassium *tert*-butoxide in deuterated *tert*-butyl alcohol[6] to afford *r*-1-ethoxycarbonyl-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane. Hydrolysis with dilute acid and resolution through the quinine salt[7] gave (+)-(1*S*,2*S*,3*S*)-2-phenyl-1,3-dideuteriocyclopropanecarboxylic acid. Conversion to the corresponding nitrile, (+)-**1**-*c*, was accomplished by way of the acid chloride and the amide.[8] Epimerization of (+)-**1**-*c* with potassium *tert*-butoxide in deuterated *tert*-butyl alcohol gave a 70:30 mixture of (+)-**1**-*c* and (−)-**2**-*t*, without racemization of (+)-**1**. The rotations in CHCl₃ of optically pure nitriles were [α]_D +369° for (+)-**1** and [α]_D −22.8° for (−)-**2**.

Thermal equilibration[9] at 242.1 °C of **1** and its cis isomer **2**, starting with either isomer, was followed by VPC; the concentration vs. time data provided values for the rate constant $(k_1 + k_2 + k_{13} + k_{23}) = 1.09 \times 10^{-5}$ s⁻¹ and the equilibrium constant $K = 0.40$.
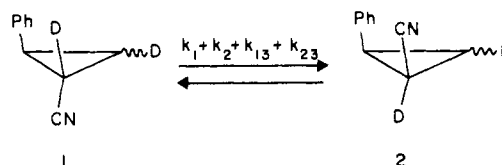
When the thermal isomerizations of **1**-*c* and of **2**-*t* were examined by VPC analysis, followed by preparative VPC separation of cis and trans isomers and NMR analysis to distinguish **1**-*c* from **1**-*t*, and **2**-*c* from **2**-*t*, the concentration vs. time data—44 experimental points—were fit to theoretical curves based on exact solutions to the kinetic expressions ap-