intensity and concentration of dioxetane at an arbitrary time $t = 0$, α = the number of acetone triplets in step 5, ϕ_T and ϕ_S are the triplet and singlet yields in steps 3 and 4, k_q is the rate constant for step 5, and τ_T is the inherent lifetime of triplet acetone under the reaction conditions and τ_D is the lifetime of **1** at the given temperature. By using $(1 - \alpha)/(\phi_S + \phi_T)$ as an adjustable parameter we obtain a "best line fit" of our data for a plot of the left-hand side of eq 6 *vs.* F/F_0.

We find that the best line fit of eq 6 with our kinetic data for **1** in degassed solution occurs for $(1 - \alpha)/(\phi_S + \phi_T) = 0.05 \pm 0.02$, thereby yielding a value of $\alpha = 0.98 \pm 0.02$. Since the values of ϕ_S and ϕ_T have been measured independently[3] and are assumed to be independent of temperature, we calculate that $k_q\tau_T$ (eq 6) is 10^3 M^{-1} (error $\pm 50\%$). These averages were determined from the linearity of plots for several runs, with the initial concentration of **1** varying from 0.3 to 1.0 *M*.

Tests for radical induced reactions proved negative. For example, decomposition of **1** (in aerated solution) in the presence of azoisobutyronitrile showed no effects on the observed rate of decay of **1**.

Equations 3–5 predict that the decay of triplet acetone concentration should also have the same time dependence as the decay of **1** itself. To establish this relationship experimentally, we followed the triplet acetone concentration by monitoring the fluorescence of 9,10-dibromoanthracene (DBA) (10^{-4} *M*), added to a degassed solution of **1** in benzene.[6] As predicted, the decay of emission of the DBA was the same as that of the concentration of **1** itself. It is important to note that the fluorescence of DBA results from triplet to singlet energy transfer;[6] however, since 10^{-4} *M* DBA quenched less than 5% of triplet acetone, the kinetics of decomposition of **1** were not significantly altered.

As a further test of steps 3–5, we predict that the decay of **1** in *degassed* solutions will be the same as that of the aerated solution when a specific triplet quencher is present. Indeed, strict first-order kinetics for decay of **1** are observed in degassed solutions containing 1 *M* 1,3-pentadiene[4] or 10^{-2} *M* 1,3-cyclooctadiene (Figure 1).

These results contrast with those found for another dioxetane system *cis*-diethoxy-1,2-dioxetane[7] (**2**). Here the decay of *indirect chemiluminescence* of anthracenes, induced by decomposition of **2**, proceeds at a faster rate but with *higher* initial intensity (followed by a lower integrated intensity) in the absence of oxygen. Without anthracenes the same rates were found for aerated and degassed solutions. It was proposed[7] that these results could be explained on the basis of sensitization of dioxetane decomposition by triplet anthracene.

In conclusion, our results provide strong evidence for occurrence of the quantum reaction sequence involving eq 5 as the key step. To our knowledge, this represents the first example of a reaction in which the chain decomposition of a molecule occurs as the direct result of interaction with its electronically excited cleavage products. The support for this chain resides in the good fit of our kinetic data to eq 6 (the rate expressions for mechanisms 3–5), the failure of radical initiations to affect the kinetics of decay of **1** and the identity of deday of DBA fluorescence to that of chemiluminescence of **1** in the absence of DBA, and furthermore in the ability of 1,3-pentadiene to restore first order kinetics for **1** in degassed solution.

Acknowledgment. The authors gratefully acknowledge the support of the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and the National Science Foundation (Grant NSF-GP-26602X).

(6) Due to the enhancement of spin–orbit coupling by the two bromine atoms, the fluorescent S_1 state of 9,10-dibromoanthracene is capable of accepting electronic energy from singlet and from triplet donors; see V. L. Ermolaev and E. B. Sveshinkova, *Opt. Spectrosc. (USSR)*, 324 (1970); V. A. Belyakou and R. F. Vassil'ev, *Photochem. Photobiol.* 11, 179 (1970).

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Formation of Platinum(II)–Oxygen and –Carbon σ-Bonded Complexes by Protonation of Cyclohexyne–Platinum(0) Complexes with Weak Protic Acids and the Nature of the β-Oxoalkyl–Platinum(II) Bond

Sir:

Acetylenes coordinated to platinum(0) are readily protonated by strong acids such as HCl and CF_3CO_2H to give platinum(II)–alkenyls[1–3] (eq 1). This property

$$Pt(RC{\equiv}CR)[P(C_6H_5)_3]_2 + HX \rightarrow PtX(CR{=}CHR)[P(C_6H_5)_3]_2 \quad (1)$$

is shared by the analogous complexes of cyclohexyne and cycloheptyne,[4] but we now report that the cyclohexyne complex $Pt(C_6H_8)$(diphos) (**1**)[5] is unique in being readily protonated by *weak* protic acids such as nitromethane, acetone, water, and methanol; the products are colorless, air-stable platinum(II) cyclohexenyls (eq 2).

$$Pt(C_6H_8)(diphos) + HX \rightarrow PtX(C_6H_9)(diphos) \quad (2)$$

2, X = p-$CH_3C_6H_4O$
3, X = CH_2NO_2
4, X = CH_2COCH_3
5, X = $CH_2COC_6H_5$
6, X = $CH(CN)(C_6H_5)$
7, X = OH
8, X = OCH_3

The reactions are carried out either in benzene at room temperature (**2**, **3** and **8**) or in refluxing toluene (**4**, **5**, **6**, and **7**). Complexes **7** and **8** represent the first nonionic mononuclear hydroxy and methoxy complexes of platinum(II) to be isolated[6] and are probably formed by an initial oxidative addition of water and

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(6) The binuclear complex $Pt_2(OH)_2[(C_6H_5)_2PO]_2[P(C_2H_5)_3]_2$, which contains bridging phosphinato groups and terminal hydroxy groups, is known: J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968). The supposed hydroxy complex $Pt(OH)[Ge(C_6H_5)_3]_2[P(C_2H_5)_3]_2$ is actually a σ-phenyl derivative, $Pt(C_6H_5)[Ge(C_6H_5)_2(OH)][P(C_2H_5)_3]_2$: R. J. D. Gee and H. M. Powell, *ibid.*, 1956 (1971).

methanol to platinum(0),[7] followed by hydrogen transfer to the coordinated cyclohexyne. Surprisingly, the methoxy complex **8** does not undergo β elimination to form a hydride even on prolonged heating, although it is rapidly converted into **7** by traces of water. In contrast, the triphenylphosphine complex $Pt(C_6H_8)[P(C_6H_5)_3]_2$ in refluxing methanol or ethanol readily forms the colorless, air-stable σ-cyclohexenyl hydrido complex *trans*-$PtH(C_6H_9)[P(C_6H_5)_3]_2$ (ir (CH_2Cl_2) 1925 cm^{-1} [ν(Pt–H)]; nmr ($CDCl_3$) δ 5.42 (broad s, 1, C=CH), −4.64 (t, 1, Pt–H, $J_{H-P\,(trans)}$ = 19.5 Hz, J_{Pt-H} = 608 Hz)), presumably *via* intermediate alkoxy complexes.[8] The reaction of **1** with methyl ketones to give **4** and **5** is catalyzed by water, and the hydroxy complex **7** is probably an intermediate. Characterization of complexes **2–8** is based on elemental analyses, nmr and ir data of which four examples are in Table I,

Table I. Spectral Data for $PtX(C_6H_9)$(diphos)

X	δ(=CH),[a] ppm	$J_{H-P(trans)}$, Hz	J_{Pt-H}, Hz	Ir,[b] cm^{-1}
CH_2COCH_3	5.14 d	10	64	1620 (ν(C=O))
$CH_2COC_6H_5$	4.94 d	9	56	1612 (ν(C=O))
OH	5.47 d	10	52	3692, 3560 (ν(OH))[c]
OCH_3[d]	5.35 d	14	51	1055 (ν(C–O))

[a] Downfield of TMS, measured in $CDCl_3$. [b] Measured in KBr disk, except where stated. [c] In $CHCl_3$. [d] $\delta(OCH_3)$ 3.43 d, $J_{H-P(trans)}$ 5.6 Hz, J_{H-Pt} = 52 Hz.

and on a single-crystal structural analysis of $Pt(C_6H_9)(CH_2COC_6H_5)$(diphos)$\cdot C_2H_5OH$ (**5**).

Crystal data are as follows: triclinic; space group, $P\bar{1}$; a = 10.16, b = 19.00, and c = 10.28 Å; α = 84.18, β = 107.09, and γ = 94.32°; Z = 2. The 4607 independent reflections, with $I/\sigma(I) \geq 3.0$, were collected on a Picker FACS-I automatic diffractometer using graphite-crystal monochromated Cu Kα radiation. Block-diagonal least-squares refinement of the overall scale factor, atomic positional parameters for all nonhydrogen atoms, anisotropic temperature factors for Pt and P, and isotropic thermal parameters for the remaining atoms have converged to a conventional R factor of 0.055. Data have yet to be corrected for absorption effects. At the present stage of refinement, bond distance esd's are: Pt–P, 0.003; Pt–C, 0.012; P–C, 0.011; C–C, 0.02 Å. The overall stereochemistry and important bond lengths are in Figure 1.

As expected, the molecule is essentially square planar about the central platinum atom, the dihedral angle between the planes defined by (Pt, P(1), P(2)) and (Pt, C(1), C(10)) being 7.3°. The atoms C(1), C(2), C(3), and C(6) are coplanar to within 0.015 Å. The Pt–C_6H_9 bond length (Pt–C(1), 2.068 (10) Å) is equal within experimental error to the Pt–C distances observed in *trans*-$PtCl[CH_2Si(CH_3)_3][P(CH_3)_2C_6H_5]_2$ (2.079 (14) Å)[9]

(7) This has precedent in the protonation of $Pt[P(C_2H_5)_3]_3$ by water and methanol: D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).

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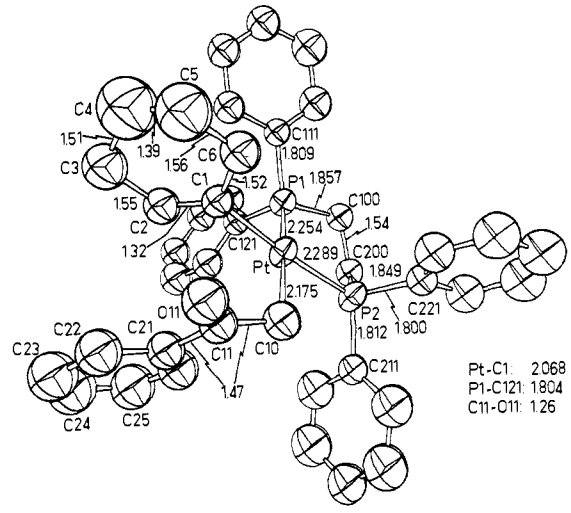

Figure 1. Stereochemistry of and important bond lengths in $Pt(C_6H_9)(CH_2COC_6H_5)$(diphos).

and *trans*-$PtCl(CH_3)[P(CH_3)(C_6H_5)_2]_2$ (2.07 (1) Å),[10] possibly because the expected shortening due to change of the trans-ligand atom from P to Cl fortuitously balances the expected lengthening due to change from sp^2- to sp^3-hydridized carbon. However, in the Pt–$CH_2COC_6H_5$ unit, the distance Pt–C(10) (2.175 (10) Å) is significantly longer than the expected value (2.10 Å), and the Pt–P distance trans to the cyclohexenyl group is significantly longer than that trans to the more weakly bonded $CH_2COC_6H_5$ group (Pt–P(1), 2.254 (3) Å; Pt–P (2), 2.289 (3) Å). Also, the distances C(10)–C(11) (1.46 (2) Å) and C(11)–O(11) (1.26 (2) Å) are shorter and longer, respectively, than the standard values (1.515 ± 0.005 and 1.215 ± 0.005 Å).[11] These trends and the low C=O stretching frequencies of **4** and **5** (Table I) suggest that the Pt–$CH_2COC_6H_5$ bond has some ionic character, with a contribution from Pt^+---CH_2=$C(C_6H_5)$=O^-, although the angle Pt–C(10)–C(11) (109°) gives no indication of rehybridization from sp^3 at the σ-bonded carbon atom. A direct ground-state β interaction of the platinum atom with π orbitals of the C=O group, which has been suggested[12] to account for the chemistry of σ alkyls of the type π-$C_5H_5Fe(CO)_2CH_2X$ (X = CO_2H, CN, CHO, or $CH{=}CH_2$), is ruled out in our case by the long Pt–O(11) distance (3.82 Å). Other distances and interbond angles in the $CH_2COC_6H_5$, C_6H_9, and diphos moieties are normal.

The results suggest that the strong σ-donor ligand array of two mutually cis phosphines and a σ-bonded alkyl[13] imparts ionicity to a platinum(II)–ligand bond and gives the metal "class A" or "hard" character. The chemical consequences of this behavior and the nature of the metal–ligand bond as deduced from ^{31}P nmr spectroscopy are currently being studied.

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Acknowledgment. We thank Johnson-Matthey Co. (United Kingdom) for a loan of platinum(II) chloride.

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Received January 22, 1973

Homogeneously Catalyzed Hydration of Nitriles to Carboxamides

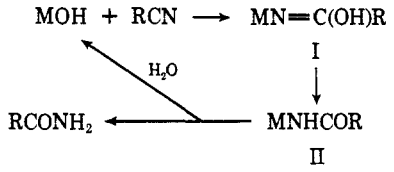
Sir:

Metal ions such as Ni^{2+} or Cu^{2+} catalyze the hydration of the C≡N function in 2-cyanopyridine[1,2] and 2-cyano-1,10-phenanthroline[3] to give the corresponding carboxamides, and the pentaamminecobalt(III) complexes of benzonitrile, and 3- and 4-cyanophenol are hydrated in alkaline solution to the corresponding *N*-carboxamido complexes.[4] Coordination through the pyridine function in the first two cases and through the nitrile function in the last case is thought to assist nucleophilic attack by hydroxide ion, although coordinated OH is also known to be effective for the hydration of aminoacetonitrile to glycine in Co(III) complexes.[5] We present a preliminary report on the hydration of simple aliphatic nitriles to the corresponding carboxamides under neutral conditions homogeneously catalyzed by planar, nonionic tertiary phosphine metal–hydroxy complexes.

A mixture of $Pt(C_6H_8)$(diphos) (**1**)[6,7] (0.067 g, 0.1 mmol), acetonitrile (5 ml), and water (2 ml) heated under reflux for 3 hr gives 0.105 g of acetamide (17 mol per mol of catalyst). The catalyst is converted into a *N*-acetamido–platinum(II) complex which has not yet been conclusively identified. Under similar conditions, $Pt(C_6H_8)[P(C_6H_5)_3]_2$[7] gives 58 mol of acetamide per mol of catalyst after 16 hr, together with the *N*-acetamido complex $Pt(C_6H_9)(NHCOCH_3)[P(C_6H_5)_3]_2$ (**3**) (40% yield based on Pt). Other catalysts for the hydration of acetonitrile include **3** (35 mol per mol, 5 hr), *trans*-$Pt(CH_3)(NHCOCH_3)[P(C_6H_5)_3]_2$ (**4**) (75 mol/mol, 2.5 hr), $Pt(C_6H_9)(OH)$(diphos)[8] (**5**) (6.8 mol/mol, 1 hr), and *trans*-$Ir(OH)(CO)[P(C_6H_5)_3]_2$[9–11] (**6**) (25 mol/mol, 20 hr). The most efficient catalyst for the hydration of acetonitrile and propionitrile is *trans*-$Rh(OH)(CO)[P(C_6H_5)_3]_2$ (**7**)[9,10] which gives 150 mol of acetamide and 200 mol of propionamide per mol of catalyst after refluxing for 3 hr. **7** also catalyzes the hydration of phenylacetonitrile, acrylonitrile, and crotonitrile to the corresponding carboxamides, but is ineffective for benzonitrile. In contrast, heating **1** under reflux with benzonitrile, water, and toluene for 15 hr gives a mixture of benzamide (0.9 mol per mol) and the *N*-benzamido complex $Pt(C_6H_9)(NHCOC_6H_5)$(diphos) (**8**) (43% yield based on Pt). In no case has further hydrolysis of the amide to the carboxylic acid been observed.

The catalytic ability of the cyclohexyne complexes **1** and **2** depends on their reaction with water to give hydroxy complexes; *e.g.*, **5** can be isolated by reaction of water with **1**.[8] The fact that *N*-amido complexes can be isolated from some of the catalytic reactions and that these complexes also function as hydration catalysts implicates them in the catalytic cycle. We suggest that the reaction involves insertion of the nitrile into the M–OH bond (Scheme I) to give an N-bonded imino–alcohol complex (I),[12] which rapidly rearranges to the *N*-amido complex (II). Addition of water to (II) regenerates the M–OH bond, thus completing the catalytic cycle. It is not known whether the insertion step involves a five-coordinate intermediate or whether hydroxide is first displaced from the coordination sphere to give an ionic complex. However, the M–OH bond is essential for the process, because *trans*-$[Pt(CH_3)(CH_3CN)\{P(C_6H_5)_3\}_2]BF_4$ does not catalyze the formation of acetamide from acetonitrile and water.

Scheme I. Catalytic Hydration of Nitriles[a]



[a] Other ligands on the metal atom M are omitted for clarity.

The platinum complex **1** differs from complexes **4**, **6**, and **7** in its ability to catalyze hydration of the olefinic double bonds of α,β-unsaturated nitriles in addition to that of the C≡N bonds. Thus, a mixture of **1** (0.067 g, 0.1 mmol), acrylonitrile (4 ml), and water (2 ml) heated at 100° for 16 hr gives 1.05 g of a mixture containing 85% β,β′-dicyanoethyl ether, 8% acrylamide, and 7% ethylene cyanohydrin, the main product presumably being derived by cyanoethylation of ethylene cyanohydrin. Under similar conditions, crotonitrile is converted into a mixture of $CH_3CH(OH)CH_2CN$ and $CH_3CH{=}CHCONH_2$, plus other as yet unidentified products.

We are currently examining the scope of these reactions using a range of nitriles and other unsaturated organic compounds. Catalysts of the type described here could prove to be a useful supplement to the usual catalysts employed for nitrile hydration, *i.e.*, acid, base, or weakly basic hydrogen peroxide,[13] if groups sensitive to these reagents are also present in the nitrile.

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(12) Compare the nucleophilic attack of methanol on coordinated pentafluorobenzonitrile in *trans*-$[Pt(CH_3)(C_6F_5CN)\{P(CH_3)_2(C_6H_5)\}_2]^+$ to give an imino–ether complex *trans*-$[Pt(CH_3)\{NH{=}C(OCH_3)(C_6F_5)\}\{P(CH_3)_2(C_6H_5)\}_2]$: H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971). These authors consider that side-on bonding of C_6F_5CN is a prerequisite for nucleophilic attack, but this seems unlikely for the aliphatic and aromatic nitriles we have studied.
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