into closer contact, approaching the sintered state[10] and rendering a minimum value for the observed resistivity. Up to 7.5% RuO_2/TiO_2, a valid quantitative trend in conductivity vs. RuO_2 loading might be expected since each sample prepared under similar conditions possesses a similar microstructure.

This communication has reported the first quantitative study of the paramagnetism of RuO_2 islands on TiO_2. It has become clear that the paramagnetic properties of surfaces have a profound effect on chemical reactions. In reaction 1 paramagnetic species are responsible for the observed catalysis since the observed reaction goes through isolated RuO_2 islands on the surface of the catalyst. A 6% RuO_2/TiO_2 loading represents the minimum concentration (under the present experimental conditions) that provides the maximum contact for paramagnetic character as well as catalytic properties.

Registry No. RuO_2, 12036-10-1; TiO_2, 13463-67-7; water, 7732-18-5.

Mechanism of Transition-Metal-Catalyzed "Double Carbonylation" Reactions. Synthesis and Reactivity of Benzoylformyl Complexes of Palladium(II) and Platinum(II)

Jwu-Ting Chen and Ayusman Sen*

Chandlee Laboratory, Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Received October 17, 1983

In recent years, there have been a number of reports[1-4] concerning the homogeneous, catalytic formation of "double carbonylation" products through the reaction of organic halides with nucleophiles in the presence of CO (eq 1). Typical catalysts

$$RX + 2CO + Y^- \xrightarrow{\text{catalyst}} RCOCOY + X^-$$

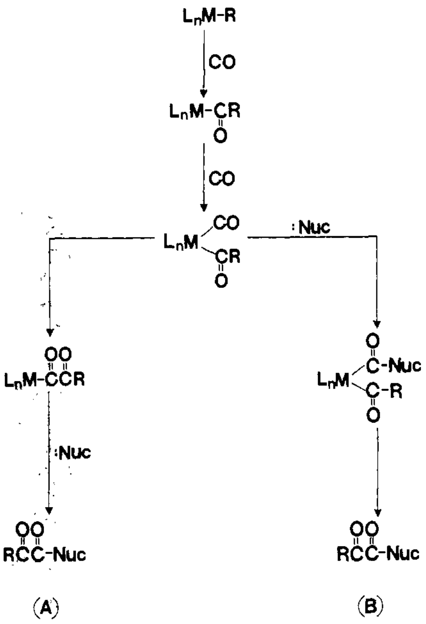
$$R = \text{hydrocarbyl};\ X = \text{halide};\ Y^- = OH^-,\ NR'^-_2 \qquad (1)$$

involved were PdX_2L_2 (L = tertiary phosphines)[1,2] and $Co_2(CO)_8$.[3,4] This reaction is intriguing from a mechanistic standpoint. The first step obviously involves the formation of a metal acyl species through the oxidative addition of the organic halide to a low-valent metal species followed by the insertion of CO into the resulting metal-carbon bond. In support of this postulate, it has been shown[5] that *trans*-$PdR(X)L_2$ reacts with CO and R'_2NH to yield $RCOCONR'_2$. We also find that *trans*-$PdCOPh(Cl)(PPh_3)_2$ (**1**) reacts analogously. Thus, the intermediacy of metal alkyl and acyl species in the "double carbonylation" reaction appears to be well supported. From the metal acyl species, however, there are two mechanistically distinct pathways to the "double carbonylation" products (Scheme I), and results reported previously do not distinguish between these routes. In this paper we present direct evidence which indicates that, at least for the palladium-catalyzed system, the "double carbonylation" products are formed by a nucleophilic attack on the coordinated CO molecule[6] of a RCO-Pd-CO species to form $RCO\text{-}Pd\text{-}CONR'_2$, which then undergoes reductive elimination to give $RCOCONR'_2$ (path B).

Table I

T, °C	$10^5 k_1$, s^{-1}	$10^5 k_2 K$, M s^{-1}
17.1 ± 0.1	8.06	0.390
25.4 ± 0.5	30.1	1.73
30.1 ± 0.1	58.1	4.32
34.2 ± 0.1	96.4	8.16

Scheme I



The central question concerning the mechanism of the "double carbonylation" reaction is the possible intermediacy of species such as $PdCOCOR(X)L_2$. Prior to our work the only known related compounds were *trans*-$PdCOCO_2CH_3(Cl)(PPh_3)_2$[7] and $MnCOCOR(CO)_5$ (R = CH_3, $PhCH_2$, Ph).[8] Since these compounds were not directly relevant to the reported palladium-catalyzed "double carbonylation" reactions, we were forced to synthesize one of the postulated intermediates, $PdCOCOPh(Cl)(PPh_3)_2$ (**2**) and its corresponding platinum analogue, **3**. As we shall demonstrate, the reactivity pattern of **2** was found to be significantly different from those of the manganese compounds, which have also been studied in some detail.[8]

The compounds **2**[9] and **3**[10] were prepared by the oxidative addition of PhCOCOCl to $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ respectively (eq 2). In the preparation of **2**, an excess of PPh_3 was added to

$$PhCOCOCl + M(PPh_3)_4 \xrightarrow{CH_2Cl_2} trans\text{-}MCOCOPh(Cl)(PPh_3)_2 \qquad (2)$$

$$\mathbf{2},\ M = Pd;\ \mathbf{3},\ M = Pt$$

the reaction mixture to retard the decomposition of the product.

For reactivity studies, **2** was chosen because of its relevance to the palladium-catalyzed "double carbonylation" reactions. In solution, at room temperature, **2** spontaneously decarbonylated to the corresponding benzoyl compound, **1**, and this reaction could be followed by ^{31}P NMR, IR, or vis spectroscopy. The decomposition rates were measured by monitoring the decrease in the intensity of the 494-nm band and in CH_2Cl_2 containing added PPh_3 (0.07-0.003 M) obeyed the following empirical rate equation

---

(1) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383.

(2) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64.

(3) Francalanci, F.; Foa, M. *J. Electroanal. Chem.* **1982**, *232*, 59.

(4) Alper, H.; Des Abbayes, H. *J. Organomet. Chem.* **1977**, *134*, C11.

(5) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1982**, *865*.

(6) Nucleophilic attack on CO coordinated to transition metals is well precedented; see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 299. For specific examples involving amines as nucleophiles, see: Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

(7) Fayos, J.; Dobrzynski, E.; Angelici, R. J.; Clardy, J. *J. Organomet. Chem.* **1973**, *59*, C33.

(8) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166.

(9) ^{31}P NMR (CH_2Cl_2) 16.5 ppm (s); IR (Nujol) $\bar{\nu}$ (C=O) 1680, 1650 cm^{-1}; vis (CH_2Cl_2) λ_{max} = 494 nm (ϵ = 80 M^{-1} cm^{-1}). Anal. Calcd for $C_{44}H_{35}O_2P_2ClPd$: C, 66.04; H, 4.38; P, 7.75. Found: C, 66.22; H, 4.50; P, 7.58.

(10) ^{31}P NMR (CH_2Cl_2) 20.27 ppm (1:4:1 triplet, $J_{Pt\text{-}P}$ = 3284 Hz); IR (Nujol) $\bar{\nu}$ (C=O) 1665, 1640 cm^{-1}. Its crystal structure will be reported separately.

0002-7863/84/1506-1506$01.50/0

(eq 3). This observed rate equation is compatible with the

$$d[\mathbf{2}]/dt = (a + b/[PPh_3])\,[\mathbf{2}] \tag{3}$$

following formal rate expression (eq 4), which may be derived

$$d[\mathbf{2}]/dt = [k_1 + k_2K/[PPh_3]]\,[\mathbf{2}] = k_{obsd}[\mathbf{2}] \tag{4}$$

from the following mechanism (eq 5) by assuming $K << [PPh_3]$.

$$PdCOCOPh(Cl)(PPh_3)_2 \xrightarrow{k_1} PdCOPh(Cl)(PPh_3)_2 + CO$$

$$PdCOCOPh(Cl)(PPh_3)_2 \overset{K}{\rightleftarrows} PdCOCOPh(Cl)(PPh_3) + PPh_3$$

$$PdCOCOPh(Cl)(PPh_3) \xrightarrow{k_2} PdCOPh(Cl)(CO)(PPh_3)$$

$$PdCOPh(Cl)(CO)(PPh_3) \xrightarrow[\text{fast}]{PPh_3} PdCOPh(Cl)(PPh_3)_2 + CO \tag{5}$$

A plot of k_{obsd} vs. $[PPh_3]^{-1}$ allowed us to obtain k_1 and k_2K from the intercept and the slope, respectively. Analysis of the temperature dependence (17.1–34.2 °C) for the decomposition of **2** (Table I) yielded these values for the Arrhenius activation parameters: k_1, $E_a = 25.8 \pm 0.7$ kcal mol^{-1}, $\ln A = 35.4 \pm 1.1$ ($\Delta H^{\ddagger} = 25.3 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9.74 \pm 0.37$ cal mol^{-1} K^{-1}); k_2K, $E_a = 31.7 \pm 0.6$ kcal mol^{-1}, $\ln A = 42.5 \pm 1.0$. Thus a significant pathway for the decarbonylation of **2** does not involve the prior dissociation of a ligand. This is in direct contrast to the behavior of the manganese compounds[8] which decarbonylate exclusively through a pathway involving prior ligand dissociation, presumbly because the latter are coordinatively saturated 18-electron complexes.

The rate of decarbonylation of **2** was unaffected at room temperature by the presence of CO up to a pressure of 700 psi. Similarly, no trace of **2** was observed when **1** was exposed to 1000 psi of CO at room temperature. These results indicated that the equilibrium constant for $\mathbf{1} + CO \rightleftharpoons \mathbf{2}$ was extremely small at room temperature, and this observation together with the observed slow rate for the decarbonylation of **2** clearly showed that the rate of the reverse reaction, i.e., $\mathbf{1} + CO \rightarrow \mathbf{2}$, must be negligible at room temperature under 15 psi of CO.

The reactions of **2** and **1** with Et_2NH are summarized below (eq 6–9). In light of these observations, we decided to react **2**

$$\mathbf{2} + Et_2NH \xrightarrow[25\ °C,\ CH_2Cl_2]{15\ psi\ CO} PhCOCONEt_2 \tag{6}$$

$$\mathbf{2} + Et_2NH \xrightarrow[25\ °C,\ CH_2Cl_2]{15\ psi\ N_2} PhCOCONEt_2 \tag{7}$$

$$\mathbf{1} + Et_2NH \xrightarrow[25\ °C,\ CH_2Cl_2]{15\ psi\ CO} PhCOCONEt_2 \tag{8}$$

$$\mathbf{1} + Et_2NH \xrightarrow[25\ °C,\ CH_2Cl_2]{15\ psi\ N_2} PhCONEt_2\ (\text{trace}) \tag{9}$$

with Et_2NH in CH_2Cl_2 at 25 °C while ^{13}CO was passed through the solution. If $PhCOCONEt_2$ was formed by path A, no incorporation of ^{13}CO was expected. However, if **2** initially underwent CO deinsertion to the benzoyl species and subsequently formed $PhCOCONEt_2$ through path B, then there should be significant incorporation of ^{13}CO next to the NEt_2 group. This was based on the expected rapid exchange between the CO bound to the benzoyl species and the externally added ^{13}CO. The product observed was >96% $PhCO^{13}CONEt_2$, as identified by GC–MS techniques. Furthermore, the observed fragments from the parent ion were $PhCO^+$ and $^{13}CONEt_2^+$. Thus we conclusively demonstrated that $PhCOCONEt_2$ was formed from **2** and Et_2NH through path B. Clearly, therefore, the palladium-catalyzed "double carbonylation" reactions must also proceed through path B. The palladium-catalyzed formation of oxalates[11] and oxamides[12] from CO and alcohols or amines, respectively, presumably also proceeds through an analogous mechanism involving the direct attack of the nucleophile on two coordinated CO molecules to give species such as $Pd(CONuc)_2$ which then undergoes reductive elimination to give the product. In a more general vein, our studies, together with the previously reported work on other systems,[8,13] indicate that a second insertion of CO into a metal acyl bond is an unfavorable step and is unlikely to occur in transition-metal-catalyzed carbonylation reactions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. This work was also partially supported by a grant from the Chevron Research Co. We also thank Johnson Matthey Inc. for a generous loan of palladium.

Registry No. 1, 50417-59-9; **2**, 88801-83-6; **3**, 88801-84-7; $Pd(PPh_3)_4$, 14221-01-3; $Pt(PPh_3)_4$, 14221-02-4; PhCOCOCl, 25726-04-9; $PhCOCONEt_2$, 34906-86-0.

Supplementary Material Available: Plots of k_{obsd} vs. $[PPh_3]^{-1}$ and $\ln k_1$ vs. T^{-1} (2 pages). Ordering information is given on any current masthead page.

---

[11] Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701.

[12] Tsuji, J.; Iwamoto, N. *Chem. Commun.* **1966**, 380.

[13] Dobrzynski, E. D.; Angelici, R. J. *Inorg. Chem.* **1975**, *14*, 59.

Effect of Ionic Strength on Acid–Base Equilibria of Charged Ions in Highly Basic Media[1]

Robert H. Schuler* and Hitoshi Taniguchi[2]

Radiation Laboratory and Department of Chemistry
University of Notre Dame, Notre Dame, Indiana 46556

Received December 9, 1983

The basicity scale H_{2-} has been introduced to describe acid–base equilibria involving deprotonation of monovalent anions in highly basic media.[3-5]

$$AH^- + OH^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} B^{2-} + H_2O \tag{1}$$

Because this scale is a modification of the H_- scale, which in effect extends the normal pH scale and was developed to describe the increased activity of OH^- at high base concentrations, one tends to consider H_{2-} as also referring to OH^- activity. Inspection of eq 1 shows that the rate constant of the forward reaction, but not that of the reverse, is expected to be ionic strength dependent. As a result the acid–base equilibrium constant $K = k_f/k_r$ should depend on ionic strength. In question are the magnitudes of the effect, particularly for equilibrium measurements on highly charged ions, and the significance of basicity scales such as H_{2-}. We demonstrate here that K for reaction 1 increases significantly with increased ionic strength. The H_{2-} basicity scale, as developed by Yagil,[4] effectively corrects measurements to zero ionic strength but is not uniquely defined by the base concentration alone. While basicity scales such as H_{2-} may be useful in empirical treatments of the concentration dependence of equilibrium data, they should not be interpreted as representing OH^- activity. Extension to scales suitable for use with more highly charged ions should be used with extreme caution.

The studies on which the above comments are based involve examination of deprotonation of carboxylated hydroxycyclohexadienyl radicals by ESR methods.[6] The experimental approaches are similar to those previously described.[7-10] The radicals

---

[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2533 from the Notre Dame Radiation Laboratory.

[2] On leave from Yamaguchi University, Yamaguchi, Japan.

[3] Bowen, K. *Chem. Rev.* **1966**, *66*, 119.

[4] Yagil, G. *J. Phys. Chem.* **1967**, *71*, 1034.

[5] A recent summary of basicity functions is given by: Cox, R. A.; Yates, K. *Can. J. Chem.* **1983**, *61*, 2225.

[6] Taniguchi, H.; Schuler, R. H., unpublished results.

0002-7863/84/1506-1507$01.50/0