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The Addition of Diphenylacetylene and of Triphenyltin Chloride to Platinum(0) Complexes. Determination of the Dissociation Constant of Tris(triphenylphosphine)platinum(0)

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We have previously described[1] the kinetics of various substitution and oxidative addition reactions of platinum(0) complexes including the reactions of $Pt(P(C_6H_5)_3)_2(C_2H_4)$ with CH_3I, $C_6H_5CH_2Br$, CH_2ICH_2I, and $C_6H_5C{\equiv}CH$ to yield the adducts $Pt(P(C_6H_5)_3)_2(CH_3)I$, $Pt(P(C_6H_5)_3)_2(CH_2C_6H_5)Br$, $Pt(P(C_6H_5)_3)_2I_2$, and $Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CH)$, respectively. It was concluded that all of these reactions proceed by dissociative mechanisms involving the coordinately unsaturated intermediate $Pt(P(C_6H_5)_3)_2$. The above investigation also led to the conclusion that the compound $Pt(P(C_6H_5)_3)_4$ is completely dissociated in benzene solution to $Pt(P(C_6H_5)_3)_3$, the further dissociation of which, to $Pt(P(C_6H_5)_3)_2$, is slight.

In this paper we describe kinetic investigations of several further reactions of platinum(0) complexes, depicted by eq 1–4. The results of these investigations support our earlier mechanistic conclusions and, furthermore, lead to a determination of the equilibrium quotient, $K_{P(C_6H_5)_3}$, for the dissociation of $Pt(P(C_6H_5)_3)_3$ according to

$$Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl \longrightarrow Pt(P(C_6H_5)_3)_2(Sn(C_6H_5)_3)Cl + C_2H_4 \quad (1)$$

$$Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC_6H_5 \longrightarrow Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5) + C_2H_4 \quad (2)$$

$$Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl \longrightarrow Pt(P(C_6H_5)_3)_2(Sn(C_6H_5)_3)Cl + P(C_6H_5)_3 \quad (3)$$

$$Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5 \longrightarrow Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5) + P(C_6H_5)_3 \quad (4)$$

$$Pt(P(C_6H_5)_3)_3 \underset{}{\overset{K_{P(C_6H_5)_3}}{\rightleftharpoons}} Pt(P(C_6H_5)_3)_2 + P(C_6H_5)_3 \quad (5)$$

Experimental Section

$Pt(P(C_6H_5)_3)_4$ was prepared from K_2PtCl_4, KOH, and excess $P(C_6H_5)_3$ in aqueous ethanol according to the procedure of Malatesta and Cariello.[2] $Pt(P(C_6H_5)_3)_2(C_2H_4)$ was prepared, through the oxide $Pt(P(C_6H_5)_3)_2O_2$, according to the procedure of Cook and Jauhal.[3] $Pt(P(C_6H_5)_3)_3$ was generated *in situ* by the addition of 1 equiv of $P(C_6H_5)_3$ to a benzene solution of $Pt(P(C_6H_5)_3)_2(C_2H_4)$, through which argon was passed to remove the displaced ethylene.[1] Diphenylacetylene (Eastman) was recrystallized from hot ethanol. Ethylene (Matheson), triphenylphosphine (Matheson, mp 80–81°), and triphenyltin chloride (M & T) were used without purification. Solutions were prepared from reagent grade benzene, deoxygenated with purified nitrogen. Diphenylacetylene and triphenyltin chloride, both as solids and in solution, were protected from light.

All of the kinetic measurements were made in benzene solution at 25°. The reactions were followed spectrophotometrically in a Cary 14 spectrophotometer with a cell compartment thermostated to ±0.3°. The rates of reactions 1, 3, and 4 were measured by following the disappearance of the reactant platinum(0) complexes (whose extinction coefficients at the indicated wavelength are given in parentheses) at 335 mμ ($4.0 \times 10^3\ M^{-1}\ cm^{-1}$), 437 mμ ($6.3 \times 10^2\ M^{-1}\ cm^{-1}$), and 415 mμ ($1.5 \times 10^3\ M^{-1}\ cm^{-1}$), respectively. The rate of reaction 2 was measured by following the appearance of the product $Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5)$ at 372 mμ ($\epsilon\ 3 \times 10^3\ M^{-1}\ cm^{-1}$), where the absorbance of the reactant, $Pt(P(C_6H_5)_3)_2(C_2H_4)$ ($\epsilon\ 3 \times 10^2\ M^{-1}\ cm^{-1}$), was small. The initial concentration of the platinum(0) complex was generally in the range 5×10^{-4} to $1 \times 10^{-3}\ M$. The initial concentration ranges of the other species were as follows (the number in parentheses refers to the equation describing the reaction): (1) 1.2×10^{-2} to $1.5 \times 10^{-1}\ M\ C_2H_4$, 3.5×10^{-3} to $1 \times 10^{-1}\ M\ (C_6H_5)_3SnCl$; (2) 2.5×10^{-2} to $1.4 \times 10^{-1}\ M\ C_2H_4$, 1.0×10^{-2} to $2.7 \times 10^{-2}\ M\ C_6H_5C{\equiv}CC_6H_5$; (3) 2.7×10^{-3} to $8.3 \times 10^{-2}\ M\ P(C_6H_5)_3$, 7.6×10^{-3} to $3.5 \times 10^{-2}\ M\ (C_6H_5)_3SnCl$; (4) 9.6×10^{-3} to $3.3 \times 10^{-2}\ M\ P(C_6H_5)_3$, 1×10^{-2} to $8 \times 10^{-2}\ M\ C_6H_5C{\equiv}CC_6H_5$.

Results and Discussion

The kinetic behavior of each of the reactions resembled that previously observed[1] for the reactions of $Pt(P(C_6H_5)_3)_2(C_2H_4)$ with CH_3I, $C_6H_5CH_2Br$, and CH_2ICH_2I. This behavior is accommodated by the mechanism depicted by eq 6 and 7, involving a pre-equilibrium dissociation of the platinum(0) complex $Pt(P(C_6H_5)_3)_2X$ (where X = $P(C_6H_5)_3$ or C_2H_4) into $Pt(P(C_6H_5)_3)_2$ and X, followed by addition of the substrate (YZ = $C_6H_5C{\equiv}CC_6H_5$ or $(C_6H_5)_3SnCl$) to $Pt(P(C_6H_5)_3)_2$. Over the extensive concentration ranges of X and YZ cited earlier, each of the reactions obeyed the rate law deduced from the above mechanism, *i.e.*

$$Pt(P(C_6H_5)_3)_2X \overset{K_X}{\rightleftharpoons} Pt(P(C_6H_5)_3)_2 + X \quad \text{(rapid equilibrium)} \quad (6)$$

$$Pt(P(C_6H_5)_3)_2 + YZ \xrightarrow{k_{YZ}} Pt(P(C_6H_5)_3)_2YZ \quad (7)$$

$$-d[Pt(P(C_6H_5)_3)_2X]_{tot}/dt = k_{YZ}K_X[Pt(P(C_6H_5)_3)_2X][YZ][X]^{-1} \quad (8)$$

where $[Pt(P(C_6H_5)_3)_2X]_{tot} = [Pt(P(C_6H_5)_3)_2X] + [Pt(P(C_6H_5)_3)_2]$. Under the conditions of our measurements, *i.e.*, with [X] and [YZ] in sufficient excess over $[Pt(P(C_6H_5)_3)_2X]$ so as to remain essentially constant during each reaction, and with [X] sufficiently high so that dissociation of $Pt(P(C_6H_5)_3)_2X$ was neg-

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[1] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968). This paper cites pertinent earlier references.

[2] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

[3] C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **90**, 1464 (1968).

TABLE I
SUMMARY OF KINETIC DATA

Reaction	$k_{YZ}K_X$,[a] sec^{-1}	k_{YZ}, M^{-1} sec^{-1}	K_X, M
$Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl$	5.0×10^{-2}	17 ± 8[b]	$(3.0 \pm 1.5) \times 10^{-3}$[c]
$Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC_6H_5$	1.2×10^{-1}	40 ± 20[b]	$(3.0 \pm 1.5) \times 10^{-3}$[c]
$Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl$	3.0×10^{-3}	...	$(1.8 \pm 0.9) \times 10^{-4}$[d]
$Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5$	5.6×10^{-3}	...	$(1.4 \pm 0.7) \times 10^{-4}$[d]

[a] In benzene at 25°; computed from slopes of plots in Figure 1. [b] Computed from experimental value of $k_{YZ}K_X$ using previously determined[1] value of $(3.0 \pm 1.5) \times 10^{-3}$ for K_X (*i.e.*, $K_{C_2H_4}$). [c] From ref 1. [d] Computed from experimental value of $k_{YZ}K_X$ using value of k_{YZ} determined above from corresponding reaction of $Pt(P(C_6H_5)_3)_2(C_2H_4)$ with YZ.

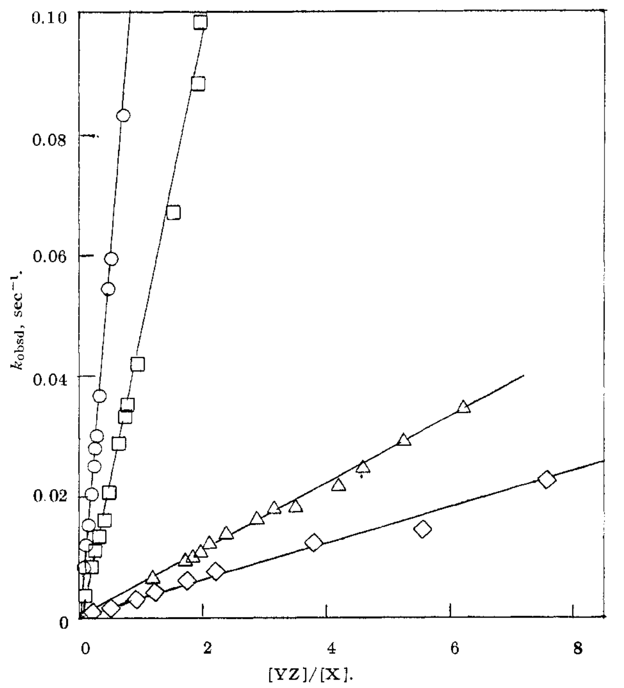

Figure 1.—Plots of k_{obsd} *vs.* [YZ]/[X] according to eq 9 for the reactions: ◇, $Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl$; △, $Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5$; □, $Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl$; ○, $Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC_6H_5$.

ligible (*i.e.*, $[Pt(P(C_6H_5)_3)_2X] \approx [Pt(P(C_6H_5)_3)_2X]_{tot}$),[4] the observed kinetic behavior was pseudo first order, *i.e.*

$$-\mathrm{d}\ln[Pt(P(C_6H_5)_3)_2X]_{tot}/\mathrm{d}t = k_{obsd} = k_{YZ}K_X[YZ][X]^{-1} \quad (9)$$

Excellent linear plots, depicted in Figure 1, of k_{obsd} *vs.* $[YZ][X]^{-1}$ were obtained for each reaction, from the slopes of which the values of $k_{YZ}K_X$ listed in Table I were derived.

An earlier determination[1] of $K_{C_2H_4}$, although of relatively low accuracy ($(3.0 \pm 1.5) \times 10^{-3}$ M), in combination with the present values of $k_{YZ}K_{C_2H_4}$, yields the values of k_{YZ} listed in Table I, *i.e.*, $k_{(C_6H_5)_3SnCl} = 17 \pm 8$ and $k_{C_6H_5C{\equiv}CC_6H_5} = 40 \pm 20$ M^{-1} sec^{-1}. These data, in combination with the values of $k_{YZ}K_{P(C_6H_5)_3}$ in Table I, lead to the determination of $(1.6 \pm 1) \times 10^{-4}$ M for $K_{P(C_6H_5)_3}$, the equilibrium quotient for the dissociation of $Pt(P(C_6H_5)_3)_3$ according to eq 5.

The available data, including those obtained in the present investigation, reveal that the reactivity of $Pt(P(C_6H_5)_3)_2$ toward various acetylenes increases in the order: $C_6H_5C{\equiv}CC_6H_5$ ($k_{YZ} = 40$ M^{-1} sec^{-1}) < $C_6H_5C{\equiv}CH$ ($k_{YZ} = 2.8 \times 10^2$ M^{-1} sec^{-1})[1] < $HC{\equiv}CH$ ($k_{YZ} = 4.6 \times 10^2$ M^{-1} sec^{-1}).[5] It is of interest that this order is opposite to that of the thermodynamic stabilities of the resulting $Pt(P(C_6H_5)_3)_2$(acetylene) complexes.[6]

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(4) The kinetic measurements on reaction 1 were also extended to lower C_2H_4 concentrations, in the range 2.5×10^{-3} to 1.2×10^{-2} M where this condition is no longer fulfilled, and a correction for the dissociation of $Pt(P(C_6H_5)_3)_2C_2H_4$ is necessary. The results of these experiments yielded a value of $K_{C_2H_4}$ of $\sim 2 \times 10^{-3}$ M, consistent with that determined earlier.[1]

(5) J. P. Birk and J. Halpern, unpublished measurements.

(6) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957)

Correspondence

The Mechanism of Carbonyl Exchange in $Mn(CO)_5X$ Compounds[1]

Sir:

The exchange of CO groups in $Mn(CO)_5X$ compounds was first extensively investigated by Wojcicki and Basolo[2] and somewhat later by Hieber and Wollmann.[3] The results of these studies, which indicated a considerable difference in the rates of axial *vs.* radial CO group exchange, have recently been called into question.[4,5] Infrared techniques have been employed to follow the rate of ^{13}CO or $C^{18}O$ incorporation into $Mn(CO)_5X$ compounds. There appears to be little or no difference in the specific rate constants for substitution at the two positions.

The mechanistic implications of these more recent

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(1) This research was supported by a grant from the National Science Foundation, GP 6396X.

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(4) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

(5) B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc., A*, 522 (1968).