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Notes

Orthometalation Reactions of Binuclear Dirhodium(II) Compounds: Thermodynamic Studies

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After the report[2] that $Rh_2(O_2CCH_3)_4(MeOH)_2$ and PPh_3 react in boiling acetic acid to give $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$, a mixed-ligand dirhodium(II) compound containing acetate and orthometalated triphenylphosphine anions, a few related compounds were reported[3] in the literature. We recently characterized[4] the intermediate monometalated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$, isolable also from the reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ and PPh_3 under slightly different reaction conditions.

It is remarkable that $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ reacts very rapidly with excess triphenylphosphine under mild conditions to give $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)_2$ in a quantitative yield.[4] If triphenylphosphine is added stepwise to $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$, the intermediate $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](PPh_3)(HO_2CCH_3)$ was formed first; this compound underwent metalation only in refluxing chloroform.[4b]

An intriguing aspect of these reactions is the fact that they usually proceed faster in the presence of acetic acid even though the metalation process involves the substitution of one acetate group by an orthometalated phosphine anion.

The possibility of having rapid and stoichiometric metalation reactions at room temperature prompted us to undergo a study of the thermodynamic parameters related to the metalation process. Up to now, a limited number of thermodynamic studies have been reported for cyclometalation reactions[5] because of the difficulty of having rapid and clean reactions at room temperature. Some complementary results concerning the reactivity and spectroscopic behavior of the compounds studied in this paper were recently published.[4b]

Experimental Section

Starting Materials. The metalated compounds $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ (**1**),[4b] $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)(PPh_3)$ (**2**),[4b] and $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ (**5**)[2] were prepared according to literature procedures. PPh_3 (Aldrich) was recrystallized from hot ethanol prior to use. Chloroform for chromatography, free of EtOH, was used and was degassed before use.

NMR Spectroscopy. ^{31}P NMR spectra were recorded on a Bruker AC-200FT spectrometer (81.015 MHz) operating at 300 K, with broad-band decoupling. The products were dissolved in chloroform, using 85% H_3PO_4 in D_2O as external reference.

Spectrophotometric Measurements and Stability Constant Determination. Reactions (A, C, D, and E (in Scheme I) have been studied by following the changes in the UV–vis spectral features brought about by titration of chloroform solutions of compound **1** or **5** with chloroform solutions of PPh_3 at 25 °C. The apparatus employed consists of a titration vessel equipped with thermostat, magnetic stirrer, and automatic buret and connected by a peristaltic pump to a thermostated 1-cm^3 quartz cell monitored on a Lambda 9 (Perkin-Elmer) spectrophotometer by a PC computer. The titration vessel, as well as the quartz cell and the tube connections (Teflon and Viton tubes), was accurately dried and then kept under an argon atmosphere. Each starting solution was prepared by weight from chloroform and compound **1** or **5**, respectively poured into the titration vessel, and allowed to circulate through the spectrophotometric cell. Successive additions of a chloroform solution of PPh_3 were performed by means of the automatic buret. The spectra of the starting solutions and of the solutions obtained after each addition were recorded from the spectrophotometer by the computer. A few minutes was required after each addition for absorbance equilibration. The equilibrium constants related to reactions A, C, D, and E were calculated from the spectroscopic data, by means of the computer program SUSPECT.[6] The values of 24 different wavelengths in the range 400–500 cm^{-1} were used as input data. The logarithms of the stability constants obtained are reported in Table I.

Microcalorimetry. The enthalpy changes for reactions A, B, E, and H, presented in Table I, were measured by means of a fully automated calorimetric system having a thermal activity monitor (Thermometric AB, Model 2277) microcalorimeter as the calorimetric unit. The calorimetric system was programmed to perform stepwise titrations. A full description of the calorimetric apparatus and of the method for determining enthalpy changes is given in ref 7. Solutions of compounds **1**, **2**, and **5** and PPh_3 were prepared using chloroform as solvent and were approximately 0.5×10^{-2} mol L^{-1}. The heats of titrations A and H were determined by adding chloroform solutions of compound **1** to the

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[6] Sabatini, A.; Vacca, A. To be submitted for publication. This program minimizes the sum of the squares residuals between the values of the experimental and calculated absorbances. The refined parameters are the equilibrium constants and the molar extinction coefficients. The Gauss–Newton method employing a full design matrix has been used. The elements of this matrix are the partial derivatives of the absorbance with respect to either the cumulative stability constants or the molar extinction coefficients. This program derives from the computer program for stability constant determination from potentiometric titrations, SUPERQUAD (Gaus, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195).

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Scheme I

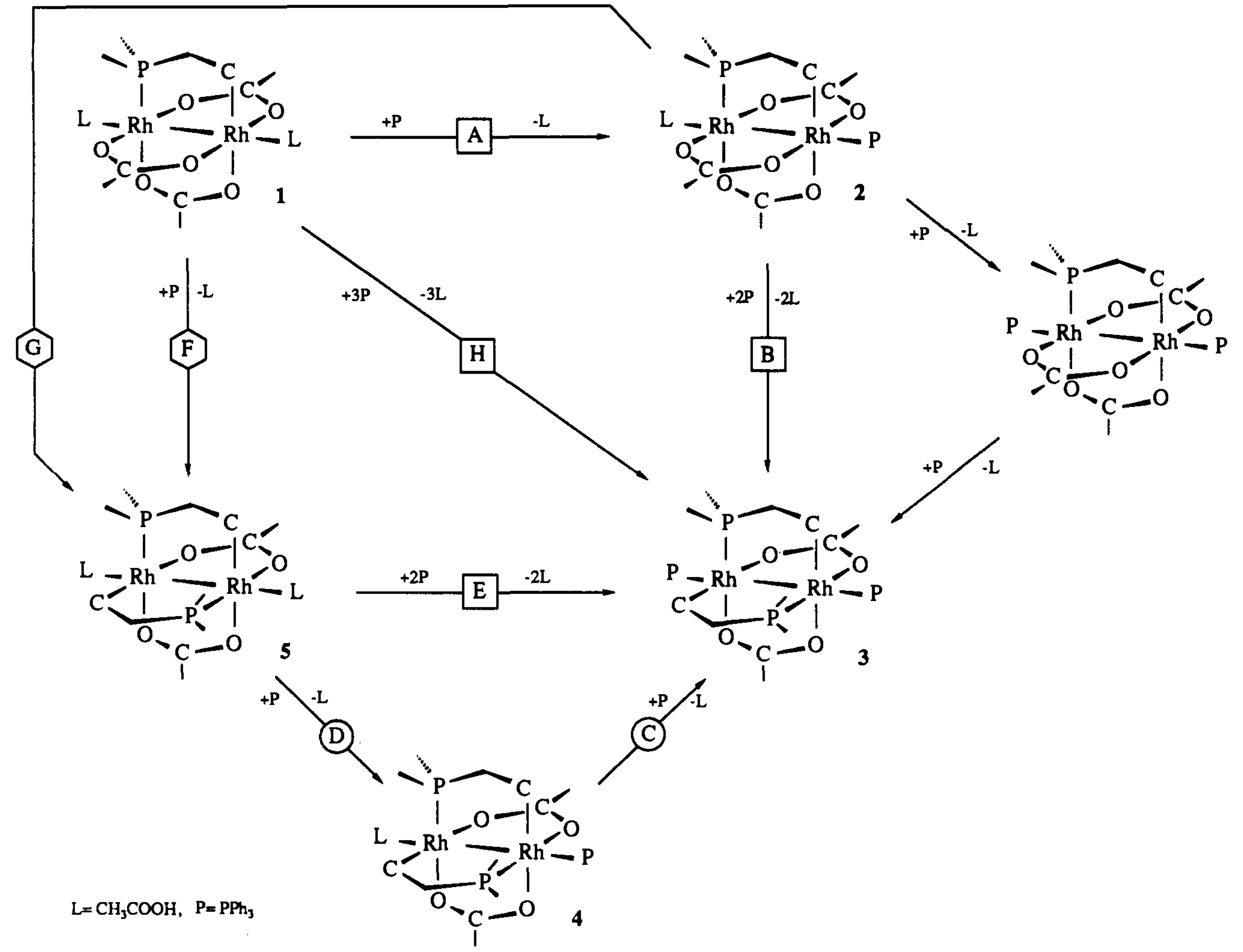

Table I. Thermodynamic Parameters for the System $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2/P(C_6H_5)_3$ Determined in $CHCl_3$ at 25 °C[a]

reacn	log *K*	$-\Delta H°$	$T\Delta S°$
A[c]	3.6 (1)	5.9 (1)	−1
B[d]		6.8 (1)	
C	1.0 (1)		
D	1.9 (1)		
E[c]	2.9 (1)	3.8 (1)	0.2
F[b,d]		8.8	
G[b,d]		2.9	
H[d]		12.6 (1)	

[a] Values in parentheses are standard deviations in the last significant figures. ΔH and $T\Delta S$ values are in kcal mol^{-1}. [b] Calculated values. [c] Equilibrium reactions. [d] Nonequilibrium reactions.

calorimetric cell and delivering successive additions of chloroform solutions of PPh_3 by means of a Hamilton gastight microsyringe. The heat of titration B was also determined in a similar way but using chloroform solutions of compound **2**. A few minutes was required for thermal equilibration after each addition: the thermal effect relative to each step was measured and recorded. Some experiments were performed in order to vary the **1**:PPh_3 molar ratio from 20:1 to 1:20. The completion of the reactions was determined on the basis of NMR and spectrophotometric results and confirmed by means of the determined stability constants when equilibrium conditions were observed. Blank experiments were performed to correct for the heats of dilution of the reacting solutions.

The enthalpy change for reaction E was determined by adding solutions of **5** (from the microsyringe) to a large excess of PPh_3 in chloroform solution (in the calorimetric cell). The only complexed species present in solution before and after mixing were **5** and **3**, respectively. Corrections for the heats of dilution of reacting solutions were applied also in this case.

On the basis of the enthalpy changes related to equilibrium reactions A and E and the heats of reactions B and H, the thermochemical cycle in Scheme I was assembled and the values for the heats of reactions F and G (Table I) were calculated.

Results and Discussion

All the studied reactions for singly and doubly metalated compounds are summarized in Scheme I.

The reaction of **1** with PPh_3 in chloroform solution at 25 °C was spectrophotometrically followed (see Experimental Section). The results obtained at increasing PPh_3:**1** molar ratio agree with two reaction steps involving **1** to produce **3**, a doubly metalated dirhodium compound with two PPh_3 molecules in the axial positions.

In a first step (reaction A, Scheme I), compound **1** reacts with one PPh_3 molecule according to an equilibrium reaction in which compound **2** is formed. Calorimetric measurements gave a value of −5.9 (1) kcal mol^{-1} (Table I) for the enthalpy change related to equilibrium reaction A. The formation of **2** in solution is accompanied by a high-field resonance in the ^{31}P NMR spectrum characteristic of an axially coordinated phosphine. From this solution, compound **2** has been isolated.[4b] The presence of well-resolved $^1J(Rh-P)$, $^2J(Rh-P)$, and $^3J(P-P')$ couplings in the ^{31}P NMR spectrum[4b] of **2** and the absence of free phosphine in solution are good indications of a relatively strong axial Rh–P bond with the equilibrium **1** ⇌ **2** lying to the right.

As previously observed, the replacement in **1** of one molecule of acetic acid by PPh_3 takes place on the less hindered rhodium atom, the one with the RhO_3C environment. From spectrophotometric measurements, a log *K* value of 3.6 (1) was obtained for reaction A. This value is in agreement with the qualitative information obtained from ^{31}P NMR spectra.[4b]

In a second step (reaction B, Scheme I), **2** reacts with two phosphine molecules to produce compound **3**. We obtained a value of –6.8 (1) kcal mol^{-1} for the heat of reaction B. The substitution of the second axial acetic acid molecule by PPh_3 is accompanied by the metalation of a second phosphine molecule and the release of a bridging acetate ligand. In the same process, the transfer of a proton between the reacting phosphine and the leaving acetate ligand takes place. Under the experimental conditions used, room temperature and nonprotic solvent, the metalation reaction is not reversible. For this reason, the overall reaction (B) is not an equilibrium reaction and, consequently, compound **3** is an out-of-equilibrium species with respect to compound **2**. We have suggested[4b] that in the first step of reaction B there is a replacement of the axial acetic acid by triphenylphosphine in compound **2** and a bis(phosphine) adduct, $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](PPh_3)_2$, is formed. This very reactive species, which cannot be spectroscopically detected, undergoes rapid metalation, forming **3**.

On the other hand, compounds **3** and **5** are related by equilibrium reactions C and D in which the compound $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)(HO_2CCH_3)$ (**4**) is present. In fact, upon stepwise addition of PPh_3 to a solution of **5**, a new and broad signal is detected in the ^{31}P NMR spectrum. There is a progressive change in the chemical shift value for this new signal from –20 to –7 ppm as the PPh_3:**5** molar ratio is increased from 0 to 10. This fact and the lack of ^1J(RH–P) coupling strongly suggest that equilibria C–E are very fast. The stability constants for the equilibrium reactions were determined by computer treatment of the spectrophotometric data ($\log K_C = 1.0$ (1); $\log K_D = 1.9$ (1); $\log K_E = 2.9$ (1)). Furthermore, we determined the enthalpy change for equilibrium reaction E (–3.8 (1) kcal mol^{-1}), allowing us to calculate the heats for reactions F (–8.8 kcal mol^{-1}) and G (–2.9 kcal mol^{-1}), which, as a matter of fact, do not take place under the experimental conditions used. Additionally, the heat for the overall reaction (H) was measured (–12.6 (1) kcal mol^{-1}) to check for the consistency of this set of enthalpy values. The thermodynamic stability of the axially substituted phosphine complexes is mainly enthalpic in nature because the entropic terms are almost negligible (reaction E) or only slightly unfavorable (reaction A).

The monometalated compound **1** shows a much greater affinity for axial coordination of PPh_3 (reaction A) than the doubly metalated compound **5** (reaction D). Both steric and electronic effects can be invoked to explain the weakening of the Lewis acidity shown by the metal centers of compound **5** with respect to **1**. Reaction A takes place at a rhodium atom with a RhO_3C coordination, considerably less hindered than the rhodium atom in compound **5**, which has RhO_2PC coordination. Furthermore, the replacement of a bridging acetate ligand by a metalated phosphine molecule increases the electronic density[8] on the two metal centers, yielding weaker interaction with Lewis bases. These effects strongly influence the enthalpy changes for base addition, as shown by reaction A, whose enthalpic contribution is significantly greater than the enthalpic contribution of the overall reaction (E), in which two PPh_3 molecules instead of one are bound. Reduced acceptor capability of **5** for coordination of a second PPh_3 molecule with respect to the first one is revealed by the marked decrease in the values of the equilibrium constants for stepwise reactions D and C ($K_D \simeq 8K_C$). On the basis of merely statistical considerations for two noninteracting metal centers, a value of $K_D/K_C = 4$ has to be expected. In earlier thermodynamic studies[9,10] dealing with a base binding to the carboxylate dimer tetrakis(butyrato)dirhodium(II) in benzene or CH_2Cl_2 solutions, K_D/K_C ratios greater than 4 were also observed. Generally, the K_D/K_C ratios were largely greater than that observed in the present work. This behavior can be explained by considering an inductive effect, brought about by base coordination, operating through the metal–metal bond to reduce the Lewis acidity of the second metal center. Nevertheless, the substitution of bridging carboxylate ligands by metalated phosphine molecules lengthens the Rh–Rh bond, weakening the cooperative interaction between the two metal atoms. For instance, it has been pointed out[11] that the inductive transfer of electrostatic properties of the base in carboxylate dimers is more effective through the shorter Mo–Mo bond than through the longer Rh–Rh bond. For these reasons, synergisms between the two metal centers are expected to be more effective in dirhodium(II) tetracarboxylate than in their derivatives containing metalated PPh_3 molecules.

Four of the reactions included in Scheme I, reactions B, F, G, and H, involve a metalation process. The heat of reaction was experimentally determined for reactions B and H and was calculated for reactions F and G. Reaction F involves only metalation without exchange of axial ligands. In all the other reactions, there is an axial ligand exchange simultaneous with the metalation process.

The formation of **5** from compound **2** is an enthalpically favored process. However, this reaction only occurs in boiling chloroform[4b] and no evidence of reaction progress is noticeable at room temperature for hours. Therefore, axial coordination of the PPh_3 ligand at room temperature is preferred to phosphine metalation, which is promoted by the presence of excess phosphie ligand (reaction B). Our experimental results suggest for reaction F the pathway described by reactions A and G, in which intramolecular metalation of the axially coordinated phosphine at room temperature is an unfavorable process from a kinetics point of view. On the other hand, phosphine metalation occurs at room temperature upon double axial substitution of the dirhodium compound **1**, probably via an intramolecular reaction involving an axially coordinated molecule.

Registry No. **1**, 125396-44-3; **2**, 143843-58-7; **3**, 125505-48-8; **4**, 143843-59-8; **5**, 91837-70-6; $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](PPh_3)_2$, 143843-60-1.

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[8] The oxidation potential values obtained by cyclic voltammetry for these two compounds support this statement: **5**,[2] $E_p = +0.90$ V; **1**, $E_p = +1.02$ V (Lahuerta, P.; Latorre, J.; Payá, J. Unpublished results).

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