# An Acid–Base Model for Mixed Metal Dimer Formation. Enthalpies of Dimer Cleavage and Adduct Formation of (π-Methylallyl)palladium(II) Chloride Dimer and a Look at Mixed Metallomers

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Abstract: From enthalpies and equilibrium constants obtained calorimetrically for the following reaction in benzene

$$[(\pi\text{-MeAllyl})PdCl]_2 + 2B \rightarrow 2[(\pi\text{-MeAllyl})Pd(Cl)(B)]$$
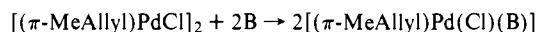
where B is a variety of Lewis bases, we have quantitatively characterized this palladium(II) Lewis acid in terms of its E_A and C_A parameters and also determined the enthalpy of dimer cleavage. In the cases of adduct formation with either a phosphine or phosphite donor, an extra-stabilization energy is observed which we attribute to stabilization from π-back-bonding. Quantitative comparisons are also made between the Lewis acidity of the Pd(II) dimer and two previously investigated Rh(I) dimers, $[(1,5\text{-COD})RhCl]_2$ and $[(CO)_2RhCl]_2$. This study constitutes an extension of our recently formulated acid–base model for mixed metallomer (molecules containing two or more metal atoms) formation. The effects of changing the metal and its oxidation state on the acidity of the metal as well as the basicity of the chloride are examined in the context of the ability of these systems to form mixed metal dimetallomers. Infrared spectroscopy and ^{13}C NMR are used to investigate the formation of mixed species.

Introduction

Considerable interest in the design and preparation of novel metal clusters and mixed metal systems for use as potential catalysts has arisen. In part I[3] of this series, general guidelines were offered for the design and synthesis of unsymmetrical mixed metallomers. Owing to their significance in the area of homogeneous catalysis,[4-7] we have chosen to quantitatively characterize and compare the Lewis acidity of some organometallic complexes of group 8 metals having a d^8 configuration. With numerous examples of Pd(II)-catalyzed reactions cited in the literature,[8] we are extending our Lewis acid–base studies to incorporate for the first time a Pd(II) Lewis acid into the E and C correlation and, thus, further test our proposed acid–base model for the formation of mixed metallomers.

The system chosen for study was bis(2-methylallyl)-μ,μ'-dichloro-dipalladium(II).[10] This dimer reacts with various Lewis bases in a reaction analogous to that previously reported for [Rh(COD)Cl]$_2$[3] and [Rh(CO)$_2$Cl]$_2$ (eq 1).[1] This reaction
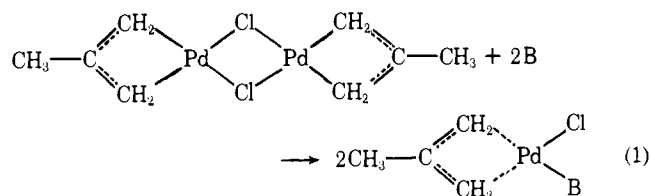
has been reported for B = phosphine,[12-23] phosphite,[16] (C$_6$H$_5$)$_3$As,[18,19,24] (C$_6$H$_5$)$_3$Sb,[18,19] amine,[25-28] DMSO,[12-14] (CH$_3$)$_2$S,[14] and isonitriles.[29] In several cases,[14,17,20-22,26-29] the adducts of (π-MeAllyl)Pd(Cl)(B) have been isolated; and an x-ray crystal structure[21] has been reported for the triphenylphosphine adduct.

From enthalpies measured in benzene, we are able to determine the constant contribution to the enthalpy of the reactions in eq 1 due to cleavage of the palladium–chloride bridge bonds and, subsequently, the "solvation-minimized" enthalpies expected for the monomer (π-MeAllyl)PdCl reacting with various Lewis bases.[3,30-32] Successful incorporation of this system into our E and C correlation[33-35] allows us to make direct, quantitative comparisons of various acid–base parameters and bridge cleavage energies between dimers where

we have not only varied substituents coordinated to the metal centers but also changed the metal and its oxidation state.

The $[(\pi\text{-MeAllyl})PdCl]_2$ system presents one further advantage over the rhodium dimers previously studied in that, for the first time, we are able to study the bridge-cleavage reaction of eq 1 for both phosphine and phosphite donors. Since E and C parameters are derived from enthalpies of interaction essentially devoid of π-back-bonding interactions, a greater value for a measured enthalpy than for an E and C calculated enthalpy is expected if there is enhanced stabilization of the adduct due to such an additional bonding contribution. Of course, one can attribute discrepancies to a particular interpretation with confidence only after a broad data base is examined, and trends are observed which are consistent with the proposed explanation. Thus far, in our E and C work, we have suggested a π-back-bonding stabilization only once before in a methylcobaloxime–phosphite[36] adduct.

Experimental Section

Materials. $[(\pi\text{-MeAllyl})PdCl]_2$,[10] $[(1,5\text{-COD})RhCl]_2$,[37] and $[(CO)_2RhCl]_2$[38] were all prepared by previously reported procedures. All other reagents were obtained and purified as previously described.[3,11]

Calorimetry and Calculations. The description of the modified calorimeter and the experimental procedure have been previously reported.[36,39] The computer program for stimultaneous determination of enthalpies and equilibrium constants has also been described.[36]

Infrared Data. Infrared spectra were obtained in C$_6$H$_6$ solution on a Beckman IR-12 instrument.

^{13}C NMR. The ^{13}C NMR spectra were recorded in d_8-toluene on a Jeol JNM-FX-60 Fourier tarnsform NMR spectrometer operating at 15 MHz. An internal ^2D lock signal was used for field stabilization. Chemical shifts were measured with internal TMS.

^1H NMR. ^1H NMR spectra were measured in both C$_6$D$_6$ and CD$_2$Cl$_2$ solutions using either a JEOLCO-C-60H high-resolution NMR spectrometer equipped with a JES-VT-2 temperature control unit or a Varian Associates HA-100 high-resolution NMR spectrometer equipped with a temperature control unit.

Mass Spectroscopy. Mass spectra were run on a Varian-MAT CH-5 mass spectrometer operating at a source temperature of 200 °C, a probe temperature of 20–40 °C, and an emission current of 1000 µA.

Table I. Thermodynamic Results for the Reaction [(π-MeAllyl)PdCl]₂ + 2B → 2(π-MeAllyl)Pd(Cl)(B) in Benzene at 24 ± 1 °C

Base	E_B	$C_B{}^a$	K^b	$-\Delta H_{measd}{}^{c,f}$	$-\Delta H_{cor}{}^{d,f}$	$-\Delta H_{calcd}{}^{e,f}$
1. Pyridine	1.17	6.40	2.3×10^3	6.3 ± 0.05	10.3^g	10.2
2. 4-Picoline	1.26	6.47^h	9.0×10^3	6.6 ± 0.05	10.6^g	10.6
3. 1-Methylimidazole	0.937	8.95	Large	9.0 ± 0.1	12.1	11.9
4. Piperidine	1.01	9.29	1.4×10^5	9.4 ± 0.3	12.5	12.8
5. Tetrahydrothiophene	0.341	7.90	8.3×10^2	5.6 ± 0.01	8.7	8.9
6. Dimethylthioformamide	0.631	9.65^i	Large	8.7 ± 0.1	11.8	11.6
7. Caged phosphite^{j,m}	0.548	6.41	Large	12.4 ± 0.2	15.5	8.2
8. Triphenylphosphine^m			Large	14.2 ± 0.1	17.3	k
9. Quinuclidine^{l,m}	0.704	13.2	Large	7.8 ± 0.2	10.9	15.3

^{a} E and C parameters taken from ref 35 unless otherwise indicated. ^{b} In units of liters/mole for the reaction $A_2 + 2B \rightarrow 2AB$. ^{c} Actual measured enthalpies uncorrected for the enthalpy of dimerization and any solvent interactions. ^{d} Enthalpies corrected for one-half the endothermic enthalpy of dimerization and for any acid interaction with benzene solvent (together, a constant correction of $W = +3.1$ kcal/mol). $-\Delta H_{calcd}$ $= -\Delta H_{measd} + W$. ^{e} Enthalpies calculated using eq 2 and $E_A = 3.41$ and $C_A = 0.98$ for (π-MeAllyl)PdCl. ^{f} In enthalpy units of kcal/mol of adduct formed. ^{g} Also corrected for 0.9 kcal/mol specific interaction of pyridine (or 4-picoline) with benzene. ^{h} Recently refined parameters taken from ref 3. ^{i} Recently obtained parameters $E_B = 0.631 \pm 0.008$ and $C_B = 9.65 \pm 0.03$ (calculated using enthalpies of adduct formation with iodine, Rh(COD)Cl, and hexafluoro-2-propanol of $-\Delta H = 10.3, 15.2$, and 8.4 kcal/mol, respectively). ^{j} Caged phosphite is 1-phospha-2,6,7-trioxa-4-ethylbicyclo[2.2.2]octane. ^{k} Using tentative parameters for trimethylphosphine ($E_B = 0.838$, $C_B = 6.55$) calculated from data limited to acids with similar C/E ratios, one can set a rough upper limit on an essentially σ interaction with $(C_6H_5)_3P$ of 10 kcal/mol. ^{l} Quinuclidine is 1-azabicyclo[2.2.2]octane. ^{m} This base was not included in the determination of E_A and C_A for (π-MeAllyl)PdCl. See text for discussion of the large discrepancy between the experimental and calculated enthalpies.

Results

The concentrations, volumes, and heat evolved for the reaction of [(π-MeAllyl)PdCl]₂ + 2B → 2[(π-MeAllyl)-Pd(Cl)(B)] in benzene are available in the microfilm edition (see paragraph at end of paper about supplementary material). The thermodynamic data are reported in Table I. E and C parameters for the bases used in this study are also listed in this table along with the enthalpies calculated from the E and C equation

$$-\Delta H = E_A E_B + C_A C_B \qquad (2)$$

where the subscripts A and B denote acid and base, respectively.[33,35] The empirically derived E and C parameters predict enthalpies devoid of any constant enthalpy contribution. Thus, the E and C calculated enthalpies should be compared to measured enthalpies corrected for the constant contributions from any solvent interactions and one-half the enthalpy of dimerization, i.e., $-\Delta H_{cor}$. Uncorrected measured enthalpies are listed in Table I under $-\Delta H_{measd}$.

E and C Parameters for (π-Methylallyl)palladium(II) Chloride Monomer. The enthalpic data for (π-MeAllyl)PdCl dimer have been treated in a manner analogous to that for the (COD)RhCl dimer.[3] Using the actual measured enthalpies shown in Table I, we have obtained the best set of acid parameters and W (the constant contribution to the enthalpy from both one-half the enthalpy of dissociation of [(π-MeAllyl)PdCl]₂ plus that from solvation) that fit the following equation:

$$-\Delta H_{measd} + W = E_A E_B + C_A C_B \qquad (3)$$

Values of $E_A = 3.41$, $C_A = 0.98$, and $W = +3.1$ kcal mol⁻¹ (calculated per mole of monomer) with marginal standard deviations of 0.37, 0.09, and 1.0, respectively, were obtained. Reasonable confidence may be placed in these parameters since bases with widely varying C_B/E_B ratios were used to determine them. Figure 1 shows the quality of the fit for E_A, C_A, and W, graphically displayed by holding W constant at 3.1 kcal mol⁻¹.

Discussion

A Comparison of the Acidity of Three Organometallic Dimers and Their Bridge Cleavage Energies. It is of interest to examine the effects of changing the metal and its oxidation state as well as the terminal substituents on the acidity of
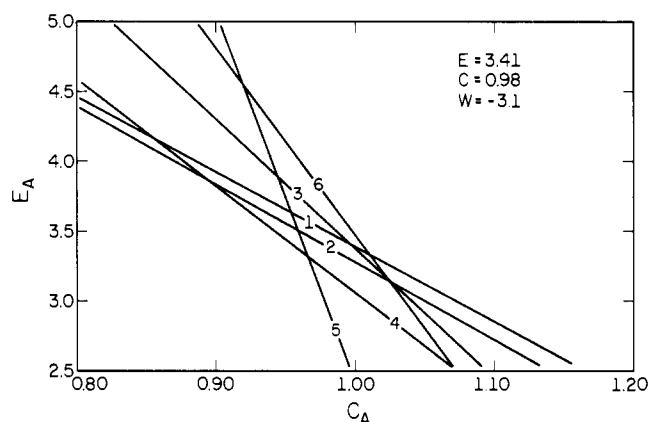

Figure 1. Plot of E_A vs. C_A for Pd(π-MeAllyl)Cl. In a few earlier articles the abscissa was incorrectly shown resulting in a positive slope for the lines in this plot. The fit illustrated and the minima obtained are not affected. Numbers refer to the bases in Table I. [In previous articles containing this type of plot, the axes have been mislabeled. For any line, the value of E must increase as C decreases and vice versa.]

chloro-bridged dimers. Table II compares our results for the interaction of [(π-MeAllyl)PdCl]₂ toward various Lewis bases with analogous results obtained for [(COD)RhCl]₂[3] and [(CO)₂RhCl]₂.[11] As can be seen from Table II, the enthalpies of adduct formation measured for [(π-MeAllyl)PdCl]₂ are slightly smaller, though comparable to those measured for [(COD)RhCl]₂. Thus, although one might expect the Pd(II) compound with its greater nuclear charge to be a stronger acid than the isoelectronic Rh(I) species, we find this effect counterbalanced by the greater σ-donating capacity of the π-methylallyl group compared with the cyclooctadiene ligand. Then in replacing cyclooctadiene with the even poorer σ-donating, but better π-accepting, carbonyl ligands, a much stronger Lewis acid is obtained in [(CO)₂RhCl]₂. The strength of these three Lewis acids is quantitatively reflected in the magnitudes of the E_A and C_A parameters shown in Table III. The energy required to cleave a mole of each dimer is twice the reported W values. Thus, it becomes successively easier to dissociate the dimers [(CO)₂RhCl]₂, [(COD)RhCl]₂, and [(π-MeAllyl)PdCl]₂ with heats of dimerization of 22.6, 12.6, and 6.2 kcal mol⁻¹, respectively. As one might expect, the strength of the Lewis acid decreases with the increasing σ-donating and/or decreasing π-accepting properties of the carbonyl, olefin, and π-methylallyl ligands, respectively.

Table II. A Comparison of Enthalpies of Adduct Formation for Chloro-Bridged Metal Dimers with Various Lewis Bases in Benzene at 24 ± 1 °C

$$[L_2MCl]_2 + 2B \rightarrow 2(L_2)M(Cl)(B)$$

	[Pd(MeAllyl)Cl]$_2$		[Rh(COD)Cl]$_2$[d]		[Rh(CO)$_2$Cl]$_2$[e]	
B	$-\Delta H_{measd}$[a,b]	$-\Delta H_{calcd}$[a,c] $- W$	$-\Delta H_{measd}$[a,b]	$-\Delta H_{calcd}$[a,c] $- W$	$-\Delta H_{measd}$[a,b]	$-\Delta H_{calcd}$[a,c] $- W$
Pyridine	7.2 ± 0.05[f]	7.1	7.6 ± 0.05[f]	7.5	12.6 ± 0.2[f]	11.8
4-Picoline	7.5 ± 0.05[f]	7.5	8.2 ± 0.1[f]	8.3	12.6 ± 0.3[f]	13.0
THTP	5.6 ± 0.01	5.8	5.3 ± 0.02	5.3	7.6 ± 0.3	7.6
DMTF	8.7 ± 0.1	8.5	8.9 ± 0.2	8.9	12.0 ± 0.1	13.4
1-MeIm	9.0 ± 0.1	8.8	9.7 ± 0.2	9.6	15.3 ± 0.1	14.9
Piperidine	9.4 ± 0.3	9.7	10.1 ± 0.06	10.3	15.7 ± 0.6	16.3
(CH$_3$)$_2$SO			3.8 ± 0.1	3.9		
DMA					5.3 ± 0.07	5.4

[a] In units of kcal mol^{-1} of adduct formed. [b] Actual measured enthalpies. [c] Enthalpies calculated from $-\Delta H_{calcd} = E_A E_B = C_A C_B$ with $-\Delta H_{measd}$ equal to $-\Delta H_{calcd} - W$. [d] Taken from ref 3. [e] Taken from ref 11. [f] Corrected for 0.9 kcal/mol specific interaction of pyridine (or 4-picoline) with benzene.

Table III. A Comparison of Acid–Base Parameters and Bridge Cleavage Energies

| Acid	E_A	C_A	C_A/E_A	W^a	P_{Cl}^b
(CO)$_2$RhCl[c]	8.72 ± 0.8	2.02 ± 0.1	0.23 ± 0.03	11.3 ± 1.1	1.4 ± 0.14
(COD)RhCl[d]	4.93 ± 0.25	1.25 ± 0.04	0.25 ± 0.02	6.3 ± 0.5	1.3 ± 0.10
(MeAllyl)PdCl	3.41 ± 0.37	0.98 ± 0.09	0.29 ± 0.04	3.1 ± 1.6	0.91 ± 0.15

[a] In units of kcal mol^{-1} of monomer. [b] Obtained from the graph in Figure 2 using W_{CO}, W_{COD}, and W_{MAP} as one-half the enthalpy of dimer formation. [c] Taken from ref 11. [d] Taken from ref 3.

Interestingly enough, though the acid strength differs for these three metal centers, their C_A/E_A ratios (or crudely the relative importance of covalent and electrostatic donor preference) do not vary significantly. In comparison with other acids in our E and C correlation, the magnitude of $C_A/E_A \approx$ 0.26 is such that one observes an enthalpic performance for sulfur donors over oxygen donors. Though the predicted enthalpy for the reaction shown in eq 1 is negative, all attempts to measure enthalpies of adduct formation either directly with dimethylcyanamide or the oxygen donors (dimethylacetamide, pyridine N-oxide) or indirectly via displacement reactions[3] using dioxane, ethyl acetate, or trimethyl phosphate as solvents were unsuccessful probably owing to an unfavorable entropy term. The free dimethylcyanamide band at 2227 cm^{-1} (ν_{CN}) remained unchanged and no new peaks appeared in the presence of [(π-MeAllyl)PdCl]$_2$,[40] indicating little or no adduct formation. It has been reported[18] that if B of eq 1 is a relatively weakly coordinating ligand such as (C$_6$H$_5$)$_3$As, (C$_6$H$_5$)$_3$Sb, or (CH$_3$)$_2$SO, a five-coordinate adduct can form even at low B/Pd ratios. The excellent fit of our data to the equilibrium expression in eq 1 would suggest that any enthalpic contribution from the presence of an effect such as this on the basis we have employed is minimal.

As can be seen from the data in Table I, the donor caged phosphite gives a substantially larger measured enthalpy than that predicted by the E and C equation. Such a result has been encountered only once before in our E and C studies and that involved an ~5 kcal mol^{-1} stabilization of a phosphite donor forming an adduct with methylcobaloxime. Since E and C parameters are obtained on systems in which the interaction is expected to be mainly σ-bond formation, the deviation found for the phosphite–methylcobaloxime adduct was attributed to stabilization of the system from metal to ligand π-back-bonding. (We include in this effect the synergistic enhancement of the σ bond.) This bonding mode would be expected to be important for phosphorus donors coordinated to 2(π-MeAllyl)PdCl, and the 7.3 kcal mol^{-1} extra stabilization over the E and C prediction is attributed to this effect. E and C parameters are not available to estimate the σ interaction with triphenylphosphine but if trimethylphosphine is used to estimate an upper limit, a 10 kcal mol^{-1} interaction is predicted

leading to a lower limit of 8 kcal mol^{-1} of π stabilization in this system.

An Acid–Base Model for Mixed Dimetallomers. We have previously developed[3] a model for predicting the enthalpies of the general reaction

$$A_2 + A'_2 \rightleftharpoons 2AA'$$
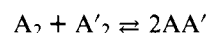
where A$_2$ was [(CO)$_2$RhCl]$_2$ and A'$_2$ was [(COD)RhCl]$_2$. The model covered A$_2$ and A'$_2$ systems in which the C_A/E_A ratio was approximately the same, so a one-parameter equation

$$-\Delta H = E_A P_{Cl} \qquad (4)$$

could be used. Figure 2 shows a fit of the experimental data for the three dimers we have now studied to eq 4. The enthalpies of adduct formation for the monomeric fragment of each dimer are plotted vs. the base parameter P_B for a given Lewis base, obtained[3] from the following equation:

$$P_B = E_B + (C_A/E_A)C_B \qquad (5)$$

The experimentally measured enthalpies employed in eq 4 are corrected for the constant contribution W, i.e., those in Table I under the heading $-\Delta H_{cor}$. The plot in Figure 2 and Table IV show the good fit of our experimental data to a one-parameter model and enable us to obtain basicity parameters for the coordinated chloride and use it to predict the enthalpy of formation of mixed metallomers.
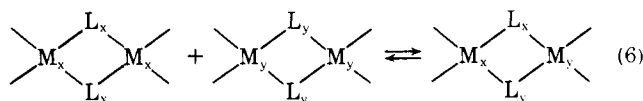
The energies required to dissociate the symmetrical dimers (i.e., twice W) and the E_A and P_B parameters describing the acidity of the monomeric fragments and the basicity of the chloride bridges, respectively, are shown in Table III. The net enthalpies expected for the above reaction of two dimers to form a given mixed dimer species are shown in Table V under ΔH_{net}. They have been calculated from the following:

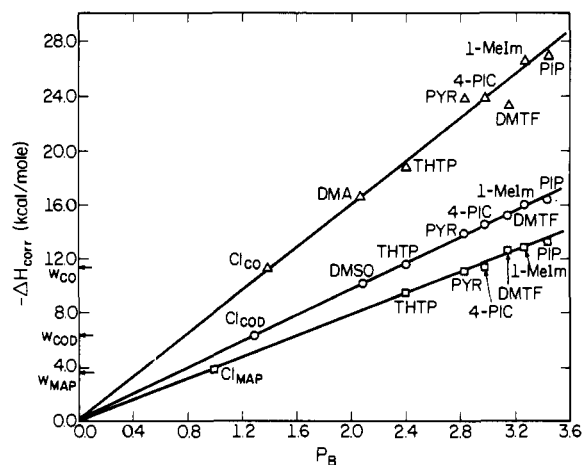$$\Delta H_{net} = 2\Delta H_{mix} + 2W_x + 2W_y \qquad (7)$$

Figure 2. A plot of corrected enthalpies of adduct formation for [M(L)Cl]$_2$ with various Lewis bases in benzene vs. a base parameter P_B. Symbols used: △, L is (CO)$_2$; O, L is (COD); □, L is (MAP) or (π-MeAllyl).

Figure 3. Comparison of the infrared spectra in benzene of Rh$_2$(CO$_4$)Cl$_2$ (—) and an equimolar mixture of Rh$_2$(CO)$_4$Cl$_2$ and Rh$_2$(COD)Cl$_2$ (- - -).

Table IV. Data Plotted in Figure 2

Base	P_B^a	[Pd(MeAllyl)Cl]$_2$ $-\Delta H_{MAP}^{b,c}$	[Rh(COD)Cl]$_2$ $-\Delta H_{COD}^{b,c}$	[Rh(CO)$_2$Cl]$_2$ $-\Delta H_{CO}^{b,c}$
Pip	3.43	13.3	16.4	27.0
1-MeIm	3.26	12.9	16.0	26.6
DMTF	3.14	12.6	15.2	23.3
4-Pic	2.97	11.4^h	14.5^h	23.9^h
Pyr	2.82	11.1^h	13.9^h	23.9^h
THTP	2.39	9.5	11.6	18.9
(CH$_3$)$_2$SO	2.08		10.1	
DMA	2.06			16.6
Cl$_{CO}$	1.4^d			11.3^g
Cl$_{COD}$	1.3^d		6.3^f	
Cl$_{MAP}$	0.91^d	3.1^e		

Plot	Theoret. slope^i	Slope found^j
$-\Delta H_{CO}$ vs. P_B	8.72 ± 0.75	7.60 ± 1.6
$-\Delta H_{COD}$ vs. P_B	4.93 ± 0.25	4.79 ± 0.26
$-\Delta H_{MAP}$ vs. P_B	3.62 ± 0.25	3.81 ± 0.51

^{a} Calculated from eq 5, $P_B = E_B + (C_A/E_A)C_B$ where $C_A/E_A = 0.26$. ^{b} Actual measured enthalpies in benzene corrected for constant contribution W. ^{c} In units of kcal mol^{-1} of adduct formed. ^{d} Obtained from the graph in Figure 2 for W_{CO}, W_{COD}, W_{MAP}. ^{e} $-W_{MAP}$, one-half the enthalpy of forming the [Pd(MeAllyl)Cl]$_2$ from monomers. ^{f} $-W_{COD}$, one-half the enthalpy of forming a [Rh(COD)Cl]$_2$ from monomers. ^{g} $-W_{CO}$, one-half the enthalpy of forming a [Rh(CO)$_2$Cl]$_2$ from monomers. ^{h} Corrected for 0.9 kcal mol^{-1} specific interaction of pyridine (or 4-picoline) with benzene. ^{i} Theory predicts a zero intercept and slope = E_A. See eq 4. ^{j} Obtained from a least-squares fit of the data. 90% confidence level. The intercepts were all zero within experimental error.

where

$$-\Delta H_{mix} = E_x P_y + E_y P_x \qquad (8)$$

W_x and W_y represent the energies required to break the symmetrical dimers, while ΔH_{mix} is an exothermic contribution to the net enthalpy from forming the unsymmetrical dimer from the monomeric fragments. Since the net enthalpies for the reactions discussed are small, the position of the equilibrium shown in eq 6 will be largely governed by entropic considerations. A purely statistical analysis leads to an equilibrium constant of 4, which corresponds to a $T\Delta S$ contribution of 0.8 kcal mol^{-1} at 298 K. Roughly the equilibrium constants should parallel the enthalpies on Table V. It should be kept in mind, however, that the model presented is tentative and in need of further testing. Synergistic effects of a decrease or increase in
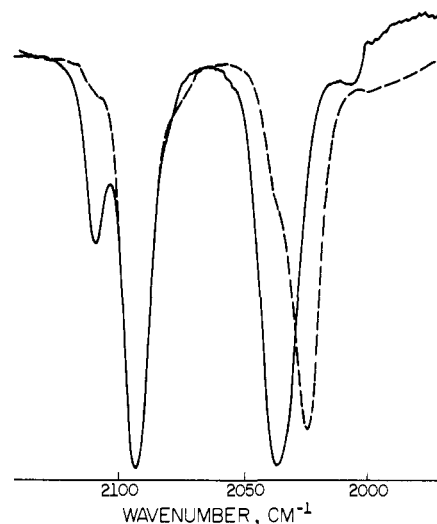
Table V. Thermodynamic Parameters^a for Formation of Mixed Dimers X$_2$ + Y$_2$ $\rightleftharpoons$ 2XY

Mixed dimer XY	$2\Delta H_{mix}^b$	$2W_x$	$2W_y$	ΔH_{net}^c
(COD)Rh<Cl,Cl>Rh(CO)$_2$	-36	12.6	22.6	-0.8 (0.6 to -2)^d
(COD)Rh<Cl,Cl>Pd(MeAllyl)	-17	12.6	6.2	2 (.2 to 3)^d
(CO)$_2$Rh<Cl,Cl>Pd(MeAllyl)	-25.4	22.6	6.2	3 (0.1 to 5)^d

^{a} In units of kcal mol^{-1}. ^{b} $\Delta H_{mix} = E_x P_y + E_y P_x$. ^{c} $\Delta H_{net} = 2W_x + 2W_y + 2\Delta H_{mix}$. ^{d} The values shown in parentheses represent upper and lower limits for the parameters calculated from the standard deviation in the numbers employed and incorporating the correlation in the uncertainties of the experimental E_A, W, and P_B parameters shown in Table III.

the basicity of the chloride of one monomeric fragment or an increase or decrease in the acidity of the other monomeric fragment upon dimer formation may exist but have tacitly been assumed absent. Geometrical constraints associated with the four-membered ring formation could also cause the model to fail.

It is interesting to point out in conjunction with the P_{Cl} parameters that although the acidity of the central metal atom is reduced in half in the course of substituting the carbonyl ligands with COD on rhodium, the P_B value of the chlorine is virtually unchanged. The further reduction in the acidity of the attached metal atom in [(MeAllyl)PdCl]$_2$ has surprisingly led to a system in which the coordinated chlorine is less basic than that on the more acidic metal centers. In view of the limited data on these systems, it is difficult to evolve any patterns in reactivity. Clearly inductive effects in inorganic systems and their transmission through metal centers are not well understood.

Tests of the Proposed Acid–Base Model for Formation of Mixed Dimers [(COD)Rh$_2$Cl$_2$(CO)$_2$]. The spectrum of an equimolar mixture of [Rh(COD)Cl]$_2$ and [Rh(CO)$_2$Cl]$_2$ in benzene provides good evidence for the existence of a mixed metallomer in solution and provides a rough measure of the equilibrium constant. This mixture is compared with that for the pure dimer [Rh(CO)$_2$Cl]$_2$ in Figure 3. The asymmetry in
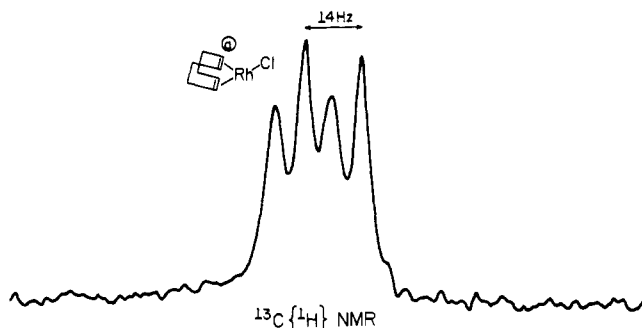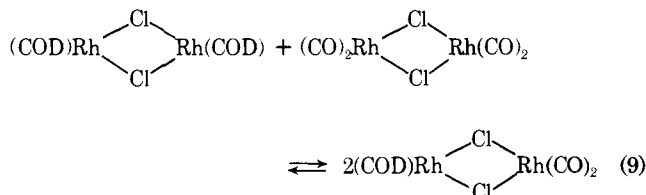
Figure 4. Low-temperature ^{13}C NMR spectra of an equimolar mixture of [Pd(MeAllyl)Cl]$_2$ and [Rh(COD)Cl]$_2$ in CD$_2$Cl$_2$. (a) Resonances assigned to COD.

Figure 5. Comparison of the infrared spectra of Rh$_2$(CO)$_4$Cl$_2$ in benzene (—) and an equimolar mixture of Rh$_2$(CO)$_4$Cl$_2$ and Pd$_2$(π-MeAllyl)$_2$-Cl$_2$ (- - -) in benzene.

the infrared peaks indicates that not only does the mixed dimer (COD)Rh$_2$Cl$_2$(CO)$_2$ form in solution but also a small percentage of the symmetrical dimers exists. A Du Pont 310 curve resolver was used on the band at 2024 cm^{-1} to obtain a rough estimate of the relative amounts of mixed metallomer and [Rh(CO)$_2$Cl]$_2$ in solution. (The [Rh(COD)Cl]$_2$ does not absorb in this region of the infrared.) From the rough relative concentrations obtained (approximately 4:1:1 of [(COD)-Rh$_2$(CO)$_2$]:[Rh(CO)$_2$Cl]$_2$:[Rh(COD)Cl]$_2$), one calculates an approximate K of 16. This is larger than the statistical prediction as would be expected if the enthalpy were negative. The predicted enthalpy (see Table V) is so small that no net heat evolution would be detected with our solution calorimeter when solutions of the symmetrical dimers are mixed and reaction 9 occurs. This is confirmed experimentally.

$$(COD)Rh\underset{Cl}{\overset{Cl}{<}}Rh(COD) + (CO)_2Rh\underset{Cl}{\overset{Cl}{<}}Rh(CO)_2$$

$$\rightleftarrows \quad 2(COD)Rh\underset{Cl}{\overset{Cl}{<}}Rh(CO)_2 \quad (9)$$

During the course of this research, synthesis of the mixed dimer (COD)Rh$_2$Cl$_2$(CO)$_2$ was reported elsewhere.[41] Following a procedure similar to that reported, a fine brown crystalline material resembling neither the golden [Rh(COD)Cl]$_2$ nor the red [Rh(CO)$_2$Cl]$_2$ was finally isolated. The resultant material could be isolated from an equimolar mixture of the parent compounds only after adding a large excess of hexane and concentrating the solution in vacuo at dry-ice temperatures overnight. Excellent analyses were obtained. The infrared spectrum in the carbonyl stretching region of the brown solid in benzene solution (2092, 2024 cm^{-1}) is close to that reported in the literature[41] for (COD)-Rh$_2$Cl$_2$(CO)$_2$ in hexadecane (2087, 2018 cm^{-1}).

[(COD)RhCl$_2$Pd(MeAllyl)]. ^{13}C {^{1}H} NMR spectroscopy was employed to investigate the following equilibrium:

[Rh(COD)Cl]$_2$ + [Pd(MeAllyl)Cl]$_2$

$$\rightleftarrows 2[(COD)RhCl_2Pd(MeAllyl)] \quad (10)$$
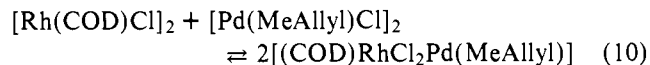
The ^{13}C {^{1}H} NMR spectra for [Rh(COD)Cl]$_2$, [Pd(MeAllyl)Cl]$_2$, and an equimolar mixture of these two dimers in CD$_2$Cl$_2$ solvent were obtained at room temperature. Table VI contains the assignments and chemical shifts of the observed resonances. The olefin carbons of the cyclooctadiene group are observed as doublets due to splitting of the carbon resonance by rhodium-103 of 100% natural abundance with a nuclear spin of $^1/_2$. At room temperature, the carbon resonances for the equimolar mixture of [Pd(MeAllyl)Cl]$_2$ and [Rh(COD)Cl]$_2$ exhibit a difference of ~2 Hz or 0.13 ppm in the chemical shifts (accurate to ±0.04 ppm) from those for each of the pure

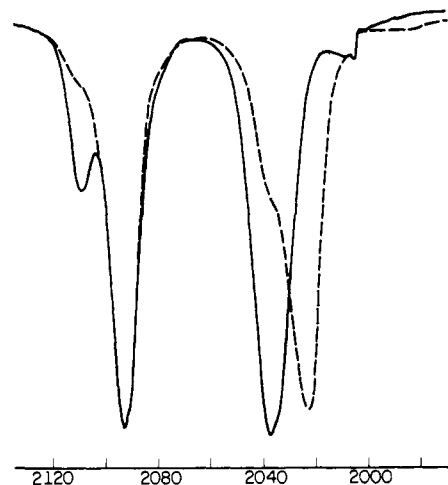symmetrical dimers. Since the two symmetrical dimers could be undergoing rapid exchange on the NMR time scale with the mixed dimer, the ^{13}C {^{1}H} spectrum of the equimolar mixture in CD$_2$Cl$_2$ was examined at −95 °C (see Figure 4). At this low-temperature limit, evidence was obtained for stopped exchange of the equilibrium shown in eq 10. Figure 4 shows the coordinated COD spectrum obtained at −95 °C for the equimolar mixture of [Pd(MeAllyl)Cl]$_2$ and [Rh(COD)Cl]$_2$ in CD$_2$Cl$_2$. The sharp doublet observed at room temperature for the olefin carbons of cyclooctadiene appears on an expanded scale in Figure 4 as a pair of broad doublets at −95 °C.

The shifts are reported in Table VI. Rough integrated intensities allow an estimate (good to within 10% at best) of the relative concentrations of the mixed dimer and [Rh(COD)Cl]$_2$ as 64 and 36%, respectively. This affords an estimate of $K = 3$ at −95 °C for eq 10. As an independent check on this estimate of the equilibrium constant, a similar examination was made of the expanded spectrum of the carbon resonances due to the central carbon of the methylallyl groups of the mixed dimer and those of [Pd(MeAllyl)Cl]$_2$. These resonances which are separated by 1.2 Hz lead to estimates of the relative concentrations of the mixed and symmetrical dimers as 62 and 38%, respectively, leading to $K = 3$. From the van't Hoff relation using the predicted ΔH_{net} value for eq 10 from Table V, the low-temperature equilibrium constant leads to a $K = 0.2$ at room temperature. Using relative concentrations of 26% mixed dimer and 37% of each symmetrical dimer estimated from the room-temperature ^{13}C NMR spectrum along with the measured chemical shifts of 79.75 and 79.22 ppm for (COD)RhCl$_2$Pd(MeAllyl) and [Rh(COD)Cl]$_2$, respectively, one can calculate the expected chemical shift of the mole-fraction weighted average resonance as 79.35 ppm compared with that observed at 79.32 ppm (the same within experimental accuracy of the chemical shifts).

The remaining carbon resonances observed in the equimolar mixture of Rh(COD)Cl]$_2$ and [Pd(MeAllyl)Cl]$_2$ at −95 °C appear as broadened resonances where the separate peaks corresponding to mixed and symmetrical dimers are not resolved. The carbon–rhodium coupling constants of 13.4 Hz observed at −95 °C for the olefin carbons are approximately the same as the 14 Hz observed at 26 °C. Comparison of the ^{13}C chemical shifts shown in Table VI for the carbon resonances of the symmetrical dimers vs. the mixed dimer (COD)RhCl$_2$Pd(MeAllyl) demonstrates that electronic effects in the dimer associated with replacing a Rh(COD)Cl fragment with a Pd(MeAllyl)Cl fragment are apparently small.

[(CO)$_2$RhCl$_2$Pd(MeAllyl)]. Infrared spectroscopy was used

Table VI. Investigation of $[Rh(COD)Cl]_2 + [Pd(MeAllyl)Cl]_2 \rightleftharpoons$ $2[(COD)RhCl_2Pd(MeAllyl)]$ $^{13}C\{^1H\}$ NMR Data in CD_2Cl_2 (see Fig 4)

Sample	T, °C	δ (in ppm from Me$_4$Si)	J_{C-Rh}, Hz
[Pd(MeAllyl)Cl]$_2$	26	$\delta_a = -127.7$	
		$\delta_b = -62.1$	
		$\delta_c = -23.0$	
[Rh(COD)Cl]$_2$	26	$\delta_d = -79.2$	14 Hz
		$\delta_e = -31.4$	
Equimolar mixture	26	$\delta_a = -127.8$	
		$\delta_b = -62.2$	
		$\delta_c = -23.0$	
		$\delta_d = -79.3$	14 Hz
		$\delta_e = -31.3$	
Equimolar mixture	-95	$\delta_{a_1} = -128.5$, $\delta_{a_2} = -128.4^a$	
		$\delta_b = -62.8$ (br)	
		$\delta_c = -23.4$ (br)	
		$\delta_{d_1} = -79.7$, $\delta_{d_2} = -79.2$	14 Hz^b
		$\delta_e = -31.1$ (br)	

^{a} (br) denotes broadened resonance. δ_{a_1} and δ_{a_2} denote chemical shifts for the tertiary carbon of the methylallyl group of the mixed and pure dimer, respectively. δ_{d_1} and δ_{d_2} denote chemical shifts for the olefin carbons of the cyclooctadiene group of the mixed and pure dimer, respectively (see text for further discussion). ^{b} The actual observed J_{C-Rh} at -95 °C was 13.4 Hz which is $\sim$14 Hz within experimental error.

to investigate the following equilibrium in benzene solution:

$$[Rh(CO)_2Cl]_2 + [Pd(MeAllyl)Cl]_2$$
$$\rightleftharpoons 2(CO)_2RhCl_2Pd(MeAllyl) \quad (11)$$
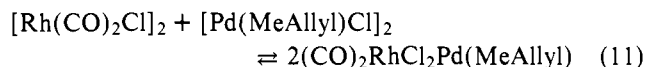
From a positive $\Delta|H|_{net}$ value predicted in Table V, one would expect very little, if any, formation of the mixed dimer species. Thus, no attempts were made to isolate such a compound. Instead, the infrared spectrum in the carbonyl stretching region was examined for a benzene solution containing equimolar amounts of the two symmetrical dimers. Figure 5 depicts a comparison between this spectrum for the equimolar mixture and the infrared spectrum for pure $[Rh(CO)_2Cl]_2$ in benzene. The similarity between Figures 3 and 5 shows that the K for this particular equilibrium is larger than that expected if the reaction in eq 9 were statistically controlled (where K would then be 4). One can make a visual order-of-magnitude estimate of $K \approx 9$ for this system.

The observed equilibria in solution are thus found to be consistent with a small (positive or negative) enthalpic contribution to the reactions in eq 9-11. The large error in our predicted enthalpy for eq 11 prohibits any attempted correlation of the equilibrium constant with the predicted enthalpies. Clearly, more work is needed in characterizing and defining other appreciably different dimer systems in order to further test our new acid-base model for mixed metal dimer formation. Our preliminary observations are not inconsistent with the model proposed.

In summary, the following principles, substantiated by our work thus far, now offer us a general guideline for the design and synthesis of mixed dimers.

For cases where the C/E ratios of two metal centers is similar and the P_B value of the bridging ligands comparable,

there will be little net enthalpic driving force for forming a mixed dimer regardless of the acid strength of the two metal centers or the relative values of C_B and E_B which lead to the same P_B. Work is presently underway in this laboratory to investigate metal dimers with very different bridging ligands and various other metal centers.

In order to maximize the enthalpic driving force for forming any mixed dimer system, it is necessary to increase the P_B parameter of the bridging atom(s) on the less acidic center and decrease the P_B parameter of the bridging ligand on the more acidic center. Only then would a strong acid center be allowed to take advantage of a more basic bridging group leading to a larger enthalpy for converting the symmetrical dimers into mixed systems.[3]

Supplementary Material Available. A listing of calorimetric data (4 pp). Ordering information is given on any current masthead page.

References and Notes

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