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The Structure of Titanium–Rhodium Heterobinuclear Complexes with μ-Phenyl Ligands[†]

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The heteronuclear μ-methylene μ-phenyl complexes $Cp_2Ti(\mu\text{-}CH_2)[\mu\text{-}p\text{-}(CH_3)_2NC_6H_4]Rh(1,5\text{-}COD)$ (**3b**) (1,5-COD = 1,5-cyclooctadiene) and $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}o\text{-}MeOC_6H_4)Rh(1,5\text{-}COD)$ (**3c**) were synthesized from $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$ (**1**) and the appropriate aromatic lithium reagent. The structure of **3b** was determined by single-crystal X-ray crystallography. The two metal atoms are bridged by the μ-methylene carbon remaining from **1** and by ipso carbon of the *p*-(*N*,*N*-dimethylamino)phenyl group. Compound **3b** crystallizes in the triclinic system, in space group $P\bar{1}$ (No. 2), with a = 8.988 (1) Å, b = 10.169 (1) Å, c = 13.707 (2) Å, α = 102.85 (1)°, β = 103.47 (1)°, γ = 101.36 (1)°, V = 1146.2 (2) Å^3, and Z = 2. The structure was solved and refined with a final R = 0.0370 by using 3882 independent reflections. Complex **3c** was shown to have a similar structure by spectroscopic comparison to **3b**.

Arenes display a number of possible bonding modes with transition metals.[1] One important class of arene–transition-metal complexes involves μ-bridges between two metal centers. This bridging structure has been suggested as an intermediate in bimolecular aryl-exchange reactions.[2] The bonding mode most often proposed for these intermediates involves a bridging ipso carbon reminiscent of the aromatic σ-complexes known as Wheland intermediates in aromatic electrophilic substitution reactions.[3] The bridging phenyl structure is analogous to that of early transition-metal benzyl complexes that contain η^2-benzyl ligands.[4]

The structures of a number of compounds containing bridging phenyl groups have been established by using NMR spectroscopy and single-crystal X-ray crystallography.[5,6] While symmetric bridging structures were observed in several homonucler clusters,[6] a few examples of asymmetric bridging structures were observed in Ta/Li, Cu/Li, Ni/Na, Os, and Li clusters.[6a,c,h,i,j] Lacking in this group of structures are compounds with bridging phenyl groups between two different transition metals. A route to such complexes is now available. Metathesis of the chloride in the previously reported titanium–rhodium μ-chloride complex, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$,[7] with an aryllithium reagent led to the formation of a heteronuclear structure containing a μ-phenyl ligand. These complexes serve as models for the interaction of arene groups with heterogeneous catalysts, such as Rh/TiO_2, which show strong metal–support interactions.[8]

Results and Discussion

The heteronuclear μ-methylene complex $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$[7] (1,5-COD = 1,5-cyclooctadiene) reacted with phenyllithium to give a thermally unstable heteronuclear μ-methylene μ-phenyl complex that was not isolable. In the analogous $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Rh(1,5\text{-}COD)$ complex,[9] the strong interaction between the Ti center and one of the CH bonds of the μ-CH_3 group indicates that the titanium center is very electron deficient. This suggests that an electron-donating group on the phenyl ring would stabilize the analogous heteronuclear μ-methylene μ-phenyl complex. As anticipated, substitution of the ortho or para position of the phenyl ring with either a methoxy or an *N*,*N*-dimethylamino group substantially increased the thermal stability (eq 1) of the resulting complexes. The room-temperature half-lives for

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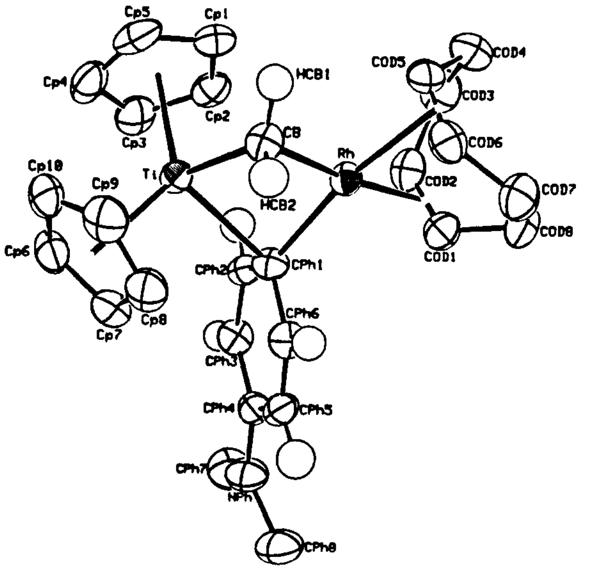
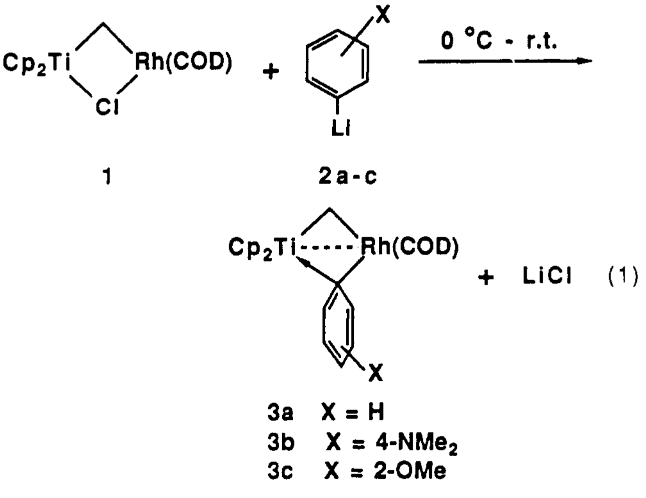


Figure 1. ORTEP diagram of complex **3b**. The ellipsoids are drawn at the 50% probability level except for the hydrogen atoms. Only the two methylene hydrogens and four phenyl aromatic hydrogens are shown.

Table I. Selected Bond Distances (Å) and Angles (deg) for 3b

Rh-Ti	2.827 (1)	HCB1-CB-HCB2	110.1 (27)
Rh-CPh1	2.122 (4)	Ti-CB-HCB1	121.7 (18)
Rh-CB	2.131 (4)	Ti-CB-HCB2	115.8 (20)
Ti-CpA	2.115 (4)	Rh-CB-HCB1	109.2 (18)
Ti-CpB	2.092 (4)	Rh-CB-HCB2	112.5 (20)
Ti-CPh1	2.403 (4)	Rh-CB-Ti	84.4 (1)
Ti-CB	2.076 (4)	Rh-CPh1-Ti	77.0 (1)
CPh4-NPh	1.377 (5)	Rh-CPH1-CPh4	148.6 (2)
CB-HCB1	0.99 (3)	CB-Rh-CPh1	96.6 (5)
CB-HCB2	0.98 (3)	CB-Ti-CPh1	89.9 (1)

the decomposition of complexes **3b** and **3c** in hydrocarbon solvents are 24 and 8 h, respectively.



Single crystals of **3b** suitable for X-ray crystallography were obtained by recrystallization from diethyl ether at −50 °C. The X-ray crystal structure of **3b** was determined, and an ORTEP diagram is shown in Figure 1. Selected bond distances and angles are given in Table I. Table II lists the data collection parameters. The molecule contains no crystallographic symmetry elements. The two cyclopentadienyl rings are coordinated to the titanium atom with Ti-ring centroid distances of 2.115 (4) and 2.092 (4) Å. The cyclooctadiene ligand is coordinated to the rhodium atom with Rh-double-bond centroid distances of 2.067 (4) and 2.055 (4) Å. The titanium atom has a pseudotetrahedral environment, while the rhodium maintains a pseudo-square-planar structure. All internal organic bond distances and angles are normal.

Table II. Crystal and Intensity Collection Data for Complex 3b

formula	$C_{27}H_{34}NRhTi$
fw	523.38
crystal color	deep green
habit	acicular
a	8.988 (1) Å
b	10.169 (1) Å
c	13.707 (2) Å
V	1145.6 (3) Å^3
λ	0.71073 Å
α	102.85 (1)°
β	115.03 (2)°
γ	101.36 (1)°
Z	2
T	21 °C
monochromator	graphite
space group	$P\bar{1}$
absences	none
crystal size	0.17 × 0.24 × 0.85 mm
μ	7.09 cm^{-1} (μr_{max} = 0.32)
diffractometer	CAD-4
θ–2θ	
2θ range	2–50°
octants collected	±*h*,±*k*,±*l*
no. of reflns measd	8323
no. of independent reflns	4031
no. with $F_o^2 > 0$	3882
no. with $F_o^2 > 3\sigma(F_o^2)$	3381
goodness of fit for merging data	1.14
final *R* index	0.0370 (0.0302 for $F_o^2 > 3\sigma(F_o^2)$)
final goodness of fit	2.09

The two metal atoms are separated by 2.827 (1) Å and bridged by the methylene carbon CB and the carbon CPh1 of the (*N*,*N*-dimethylamino)phenyl group. The distance between the two metal atoms is essentially equivalent to the Ti-Rh distance in the μ-methylene μ-methyl analogue (2.835 (1) Å)[9] and is shorter than the Ti-Rh distance in the μ-methylene μ-chloride analogue (2.986 (1) Å).[7b] The Ti-Rh separation of 2.827 (1) Å is sufficiently short such that a direct metal-metal interaction is possible. For comparison, the Ti-Rh distance in an alloy of the metals[10] is 2.68 Å and the Ti-Rh distance in a highly reduced Rh on titania is 2.55 Å.[11] The Ti-CB bond length of 2.076 (4) Å is shorter than that of the μ-methylene μ-methyl analogue (2.147 (5) Å) and is longer than that of the μ-methylene μ-chloride analogue (2.015 (2) Å). However, the similar J_{CH} values (129–128 Hz) found for all of the μ-methylene groups suggest that very similar bonding of the μ-methylenes exists in these complexes. (See ref 7b and 12 for further discussion.) The calculated bond length for a Ti=CH$_2$ double bond is 1.85–1.88 Å,[13] and the measured Ti—C single bond distance in $Cp_2TiCH_2C(CH_3)_2CH_2$ is 2.15

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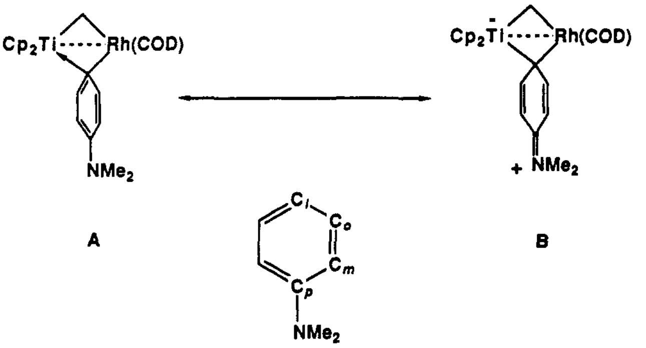


Figure 2. Two resonance structures of complex **3b** and the phenyl group showing the atomic labeling used when evaluating the nature of the aryl bonding in complex **3b**.

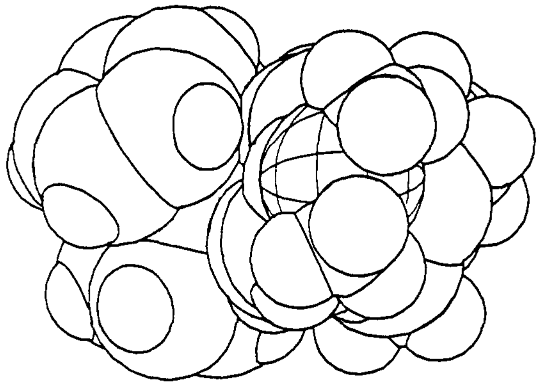
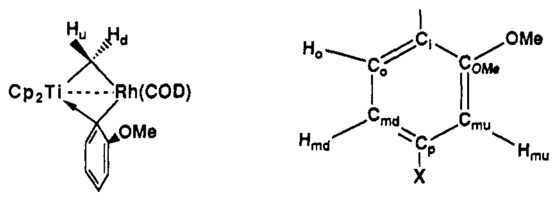


Figure 3. Space-filling model of complex **3b** generated by Biograf software with an Evans and Sutherland PS 340 system. The five-membered rings on the left side are the cyclopentadienyl groups. The lined area represents the nitrogen atom.



3c

Figure 4. Numbering system for complex **3c**: H_u and Cp_{up} represent the μ-methylene proton and the cyclopentadienyl protons nearest to the methoxy group.

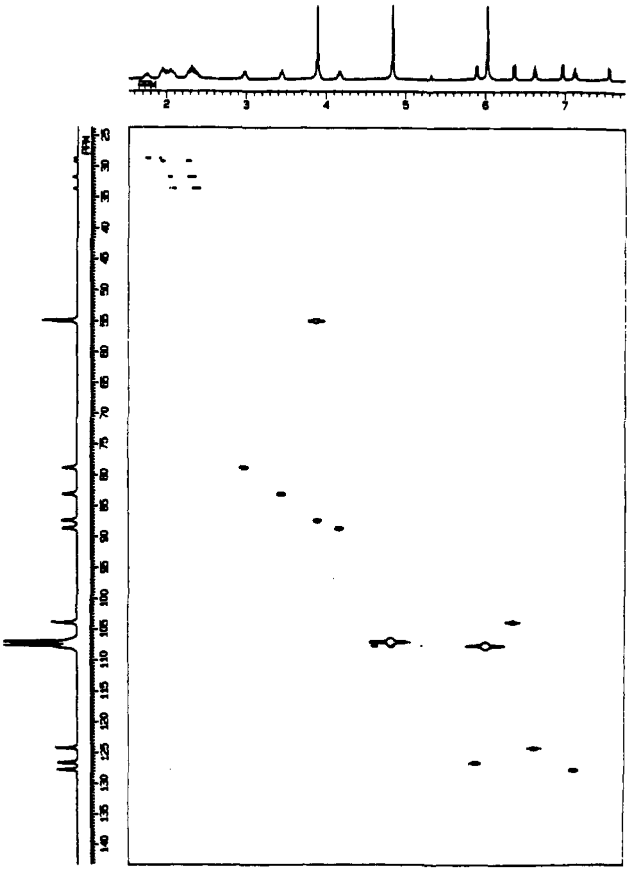


Figure 5. Heterocorrelated two-dimensional NMR of complex **3c**. ^1H NMR and ^1H-decoupled ^{13}C NMR spectra are plotted along the x and y axes, respectively.

Å.[14] The observed bond length of 2.076 (4) Å suggests that some residual multiple-bond character remains between the Ti and CH_2 group in the complex. The Rh-CB and Rh-CPh1 bond lengths of 2.131 (4) and 2.122 (4) Å are slightly longer than the average Rh-C bond distance (2.09 Å) of terminal methyl groups.[15] The Ti-CPh1 bond length of 2.403 (4) Å is significantly longer than that of the μ-methylene μ-methyl analogue (2.294 (6) Å), which retains a strong interaction between a C-H bond on the μ-methyl group and the titanium. The four central atoms are not coplanar; the dihedral angle between the Rh, Ti, CB and Rh, Ti, CPh1 planes is 145 (6)°. The plane of the phenyl ring is 16 (4)° from being perpendicular to the Rh, Ti, CPh1 plane, and the Rh-CPh1-CPh4 angle is 148.6 (2)°. The two hydrogen atoms of the bridging methylene group are tilted slightly toward the rhodium atom so that the average Ti-CB-HCB angle is 119 (2)° and the average Rh-CB-HCB angle is 111 (2)°. The dihedral angle between the Ti, CB, Rh plane and the HCB1, CB, HCB2 plane is 94 (6)°.

The C-C bonds lengths of the phenyl group were used to evaluate which of the two extreme structures, A and B (see Figure 2), best represents the structure of **3b**.[16] The average C-C bond distance of C_i-C_o and C_m-C_p (=d1) is 1.408 Å, and that of C_o-C_m (=d2) is 1.376 Å. These values more closely resemble those of p-(*N*,*N*-dimethylamino)-benzoic acid (d1 = 1.406 Å, d2 = 1.381 Å)[17] than those of *p*-nitroso-*N*,*N*-dimethylaniline (d1 = 1.404 Å, d2 = 1.348 Å),[18] which is believed to have a quinoid structure involving considerable charge-transfer character. Hence, structure A is the best representation of the bonding of the phenyl group in **3b**.

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Table III. Differential Nuclear Overhauser Effect for Complex 3c

irradiation	differential NOE, %	
Cp_{down}	H_o	3.7
Cp_{up}	H_{mu}	1.9
OMe	H_{mu}	3.1
H_o	H_{md}	2.3

A space-filling model constructed from the X-ray crystallographic data was drawn by Biograf software with an Evans and Sutherland PS 340 system. As shown in Figure 3, rotation of the (*N*,*N*-dimethylamino)phenyl group is inhibited by negative steric interactions. Most importantly, there is a very high energy barrier to rotation imposed by the required breaking of the Ti–μC bond. Very fast vertical movement of the phenyl ring is proposed to explain the single signal for the cyclopentadienyl protons and μ-methylene protons in the ^1H NMR spectrum even at −80 °C.[19]

In contrast, **3c** showed inequivalent cyclopentadienyl and methylene hydrogens in the ^1H NMR spectrum due to the asymmetry imposed by the *o*-methoxy group on the phenyl ring. Differential NOE NMR spectroscopy gave results that were consistent with **3c** having a structure analogous to **3b**. Modest but selective NOE effects were observed on irradiation of the different cyclopentadienyl groups. (See Table III and Figure 4.) A ^{13}C–^1H-correlated two-dimensional NMR spectrum (Figure 5) was used to unambiguously assign the peaks in the ^{13}C NMR spectrum.

The ^{13}C NMR chemical shift of the ipso carbon (CPh1) of **3b** is 156.7 ppm, which is downfield relative to that of the para carbon of *N*,*N*-dimethylaniline (117.2 ppm).[20] For **3c**, a similar downfield shift of the ipso carbon relative to the chemical shift of the ortho carbon of methoxybenzene (175.1 ppm vs 113.2 ppm) was observed. These downfield shifts in the ^{13}C NMR spectrum are comparable with those of ipso carbon resonances in terminal rhodium and titanium phenyl compounds.[21] This phenomenon is in contrast with the upfield shift[4a,b] or insensitivity[4c] of the resonances for the ipso carbon of the related η^2-benzyl-transition-metal complexes.

Conclusion

The structures of two titanium–rhodium heterobinuclear complexes with an ipso-μ-phenyl ligand have been determined by X-ray crystallography and differential NOE spectroscopy. This appears to be the first extensive structural study of asymmetric, bridging ipso-phenyl groups. The structures of these complexes serve as a model for the possible bonding mode of arenes in systems which show strong metal–support interactions.

Experimental Section

General. All manipulations of air- and/or moisture-sensitive compounds were carried out by using standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 catalyst (Chemalog) and Linde 4-Å molecular sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glovebox equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold freezer.

Toluene and diethyl ether were stirred over CaH_2 and then vacuum transferred from a purple solution of sodium benzophenone ketyl. Dried solvents were vacuum transferred into dry glass vessels equipped with Teflon valve closures and stored under argon. Toluene-d_8 (Cambridge Isotopes) was dried and vacuum transferred from a purple sodium benzophenone ketyl solution. Dichloromethane-d_2 (Cambridge Isotopes and Norell, Inc.) was dried over CaH_2 or Na–Pb alloy and degassed by several freeze–pump–thaw cycles. Tebbe's reagent[22] and $Cp_2TiCH_2C(CH_3)_2CH_2$ [1,1-cyclobutadienyl-3,3-dimethyltitanacyclobutane][14] were prepared as previously described.

NMR spectra were recorded on Varian EM-390 (90 MHZ, ^1H), JEOL FX-90Q (89.60 MHz, ^1H; 22.53 MHz, ^{13}C), or JEOL GX-400 (399.65 MHz, ^1H; 100.4 MHz, ^{13}C) instruments. Chemical shifts are reported in δ and referenced to residual solvent signals. Elemental analyses (C,H,N) were performed by the California Institute of Technology Analytical Services.

Synthesis of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}p\text{-}Me_2NC_6H_4)Rh(1,5\text{-}COD)$ (3b). The starting material, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$, was prepared by the reported method.[7] A mixture of β,β-dimethyltitanocene cyclobutane (0.40 g, 1.61 mmol) and $[Rh(1,5\text{-}COD)Cl]_2$ (0.40 g, 0.81 mmol) was dissolved in 30 mL of toluene at room temperature, stirred for 10 min and dried in vacuo to yield a red powder. (The yield was 57% based on ^1H NMR spectroscopy.) 4-Bromo-*N*,*N*-dimethylaniline was added dropwise to an ether suspension of lithium chips. After the reaction was complete, the solution was filtered and the solvent was removed, yielding a white powder. The lithium compound was titrated with *sec*-butyl alcohol using 1,10-phenanthroline as the indicator.[23] At 0 °C, *p*-(dimethylamino)phenyllithium (745 mg, 3.2 mmol) dissolved in 30 mL of diethyl ether was added to a 30-mL toluene solution of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$ generated as described above. ^1H NMR analysis with an internal standard showed that the yield for the second step was 33% after stirring for an hour at 0 °C. After the resultant green solution was evaporated to dryness, the product was extracted with toluene (30 mL) at 0 °C. The solution was filtered through a filter-paper-tipped cannula and then evaporated to dryness. Three recrystallizations from diethyl ether at −50 °C gave analytically pure dark green crystals of **3b** suitable for an X-ray crystallographic study. The average yield, based on the amount of 1,1-cyclobutadienyl-3,3-dimethyltitanacyclobutane, was 10%. ^1H NMR (CD_2Cl_2, −20 °C) δ 7.46 (d, 2 H, $C_6H_4NMe_2$, J = 8.7 Hz), 6.92 (s, 2 H, μ-CH_2), 6.26 (d, 2 H, $C_6H_4NMe_2$, J = 8.7 Hz), 5.53 (s, 10 H, Cp), 3.87 (m, 2 H, olefinic COD), 3.30 (m, 2 H, olefinic COD), 2.90 (s, 6 H, NMe_2), 2.27 (m, 2 H, COD), 2.13 (m, 2 H, COD), 1.90 (m, 2 H, COD), 1.82 (m, 2 H, COD); ^{13}C NMR (CD_2Cl_2, −10 °C) δ 189.4 (dt, J_{CH} = 129, J_{CRh} = 23.5 Hz, μ-CH_2), 156.7 (d, J_{CRh} = 29.4 Hz, C_i), 151.4 (s, C_p), 143.7 (d, J_{CH} = 156 Hz, C_o), 108.8 (d, J_{CH} = 157 Hz, C_m), 108.2 (d, J_{CH} = 173 Hz, Cp), 81.5 (d, J_{CH} = 156 Hz, olefinic COD), 81.4 (d, J_{CH} = 156 Hz, olefinic COD), 40.0 (quartet, J_{CH} = 136 Hz, NMe_2), 31.2 (t, J_{CH} = 126 Hz, COD), 31.1 (t, J_{CH} = 126 Hz, COD). Anal. Calcd for $C_{27}H_{34}NRhTi$: C, 61.96; H, 6.55; N, 2.68. Found: C, 61.82; H, 6.42; N, 2.78.

Synthesis of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}o\text{-}MeOC_6H_4)Rh(1,5\text{-}COD)$ (3c). 2-Iodoanisole and lithium chips were used to prepare *o*-methoxyphenyllithium powder as described above. The moisture-sensitive and thermally unstable product was stored at −35 °C in a N_2-filled glovebox. A mixture of recrystallized $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$ (0.50 g, 1.14 mmol) and *o*-methoxyphenyllithium (376 mg, 1.171 mmol) was dissolved in 15 mL of toluene and 15 mL of diethyl ether at room temperature. ^1H NMR analysis with an internal standard showed that the yield was 58% after the mixture had stirred for 30 min at room temperature. The resultant green solution was evaporated to dryness, and the product was extracted with toluene (15 mL) at 0 °C. The solution was filtered through a filter-paper-tipped cannula, evaporated to dryness, and washed with 25 mL of diethyl ether. The remaining green solid was dissolved in 10 mL of toluene and filtered again through a filter-paper-tipped cannula. After the toluene solution was concentrated to 5 mL, pentane (20 mL) was added to make a double layer. The toluene/pentane solution was cooled to −50 °C to yield green crystals. A second recrystallization at

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[19] A symmetric molecular structure in the solution state can be an alternative explanation.

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–50 °C using toluene and pentane gave analytically pure dark green crystals of **3c**. The average yield based on the amount of $Cp_2Ti(\mu-CH_2)(\mu-Cl)Rh(1,5-COD)$ was 18%. ^1H NMR (CD_2Cl_2, –10 °C) δ 7.58 (d, 1 H, J_{CH} = 7.3 Hz, H_u), 7.13 (t, 1 H, H_{pa}), 6.98 (d, 1 H, J_{CH} = 7.3 Hz, H_d), 6.62 (t, 1 H, H_{md}), 6.36 (d, 1 H, J_{CH} = 7.8 Hz, H_{mu}), 6.02 (m, 5 H, Cp_{down}), 5.89 (d, 1 H, J_{CH} = 6.8 Hz, H_0), 4.84 (m, 5 H, Cp_{up}), 4.17 (m, 1 H, olefinic COD), 3.89 (s, 3 H, OMe), 3.89 (m, 1 H, olefinic COD), 3.46 (m, 1 H, olefinic COD), 2.99 (m, 1 H, olefinic COD), 2.42–2.28 (m, 4 H, COD), 2.06–1.92 (m, 4 H, COD); ^{13}C NMR (CD_2Cl_2, –10 °C) δ 197.8 (dt, J_{CH} = 130, J_{CRh} = 22 Hz, μ-CH_2), 175.1 (d, J_{CRh} = 31.5 Hz, C_i), 171.7 (s, C_{OMe}), 127.8 (d, J_{CH} = 159 Hz, C_{pa}), 126.8 (d, J_{CH} = 156 Hz, C_o), 124.3 (d, J_{CH} = 162 Hz, C_{md}), 104.0 (d, J_{CH} = 157 Hz, C_{mu}), 107.8 (m, J_{CH} = 172 Hz, Cp), 107.2 (m, J_{CH} = 174 Hz, Cp), 88.7 (dd, J_{CH} = 157, J_{CRh} = 8.8 Hz, olefinic COD), 87.6 (dd, J_{CH} = 156, J_{CRh} = 8.1 Hz, olefinic COD), 78.9 (dd, J_{CH} = 149, J_{CRh} = 8.1 Hz, olefinic COD), 31.9 (t, J_{CH} = 128 Hz, COD), 29.9 (t, J_{CH} = 125 Hz, COD), 29.4 (t, J_{CH} = 130 Hz, COD), 28.9 (t, J_{CH} = 127 Hz, COD). Anal. Calcd for $C_{26}H_{31}OTiRh$: C, 61.19; H, 6.12. Found: C, 61.35; H, 6.03.

Crystal Structure Determination of $Cp_2Ti(\mu-CH_2)(\mu-p-Me_2NC_6H_4)Rh(1,5-COD)$. A dark green acicular crystal of $Cp_2Ti(\mu-CH_2)(\mu-p-Me_2NC_6H_4)Rh(1,5-COD)$ was mounted in a thin-walled glass capillary under nitrogen. Table II lists the data collection parameters. The rhodium atom was found from a Patterson map; the coordinates of the other non-hydrogen atoms were obtained by successive structure factor–Fourier calculations. Hydrogen atoms were initially placed by computation or difference maps and subsequently refined.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference (*International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, pp 71, 149). $R = \sum|F_o - F_c|/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned based on counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. No absorption or secondary extinction corrections were required.

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Supplementary Material Available: Tables listing final parameters, complete distances, complete angles, and anisotropic displacement parameters (6 pages); a table of structure factors (16 pages). Ordering information is given on any current masthead page.

First Structurally Characterized Cis Acyl Carbamoyl Complexes of Platinum(II). Model Study of Palladium-Catalyzed Double-Carbonylation Reactions

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Neutral acyl carbamoyl complexes of platinum(II), *cis*-$Pt(COPh)(CONR_2)(PPh_3)_2$ (R = Me (**3a**), Et (**3b**)), were prepared by nucleophilic attack of $LiNMe_2$ and Et_2NH, respectively, at the CO ligand of *cis*-$[Pt(COPh)(CO)(PPh_3)_2](BF_4)$ (**2**), generated in situ by Ag^+-induced CO deinsertion from *trans*-$Pt(COCOPh)(Cl)(PPh_3)_2$ (**1**). NMR data show that four methylene hydrogens in the carbamoyl ligand of **3b** are diastereotopic. The single-crystal structure of complex **3b**, determined by X-ray diffraction, is a distorted square plane with ∠C1–Pt–C6 = 79.6 (5)°. Such a peculiar small angle causes the distinguishing close distance (only 2.63 (2) Å) between the two carbonyl carbon atoms C1 and C6, which presumably facilitates reductive elimination of the acyl and carbamoyl ligands to yield the double-carbonylated α-keto amide.

Introduction

Acyl carbamoyl complexes, RC(O)–M–C(O)NR′$_2$, have been proposed as key intermediates in palladium-catalyzed double-carbonylation reactions, which lead to the formation of α-keto amides.[1] Previous mechanistic studies suggested that acyl carbamoyl species could be formed via a nucleophilic attack at a coordinated CO ligand of an acyl carbonyl complex, RC(O)–M–C(O), either by an amine or by an amide.[2] The acyl and carbamoyl groups, if in a cis arrangement, would then facilitate the subsequent reductive elimination to give the double-carbonylated products[3] (Scheme I). However, only a very small number of acyl carbamoyl complexes of Pd(II) and their analogues of Pt(II) have been reported.[4] An acyl alkoxycarbonyl derivative of Pt(II) has been synthesized by nucleophilic

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