trum was a slight broadening of the signals, so there is no evidence of interconversion of the two isomers at this temperature; this suggests a *lower* limit to the alkyne rotation barrier of ca. 20 kcal $mol^{-1}$. This is in sharp contrast with observations on related vertical $(C_5Me_5)$ benzyne derivatives of Nb and Ta, where an *upper* limit to benzyne rotation was estimated around 9 kcal $mol^{-1}$ ($(C_5Me_5)TaMe_2(C_6H_4)$).[4a] For the more general horizontal geometry (with the alkyne axis parallel to the $C_5Me_5$ plane) the barrier to alkyne rotation in one example, $(C_5Me_5)Ta(Cl)(OMe)(PhC\equiv CPh)$, is 11 kcal $mol^{-1}$ ($^{13}C$ NMR data).[2a] The computed barrier is around 6 kcal $mol^{-1}$ in the symmetrical model complex $CpNbCl_2(HC\equiv CH)$(EHMO calculations).[3b]

Thus, these results suggest that when a Tp$'$ ligand replaces a cyclopentadienyl ligand in these group 5 four-electron-donor alkyne complexes, the ground-state structure, in both the solid state and in solution, adopts the vertical geometry. Furthermore, the energy difference between the two orthogonal alkyne orientations increases substantially. The physical basis for this behavior is probably both electronic and steric, but since the bonding parameters for coordinated alkynes in all of the known X-ray structures, regardless of whether the alkyne is perpendicular or parallel, are so similar, we believe that the main contribution is steric. The utilization of these properties in organic transformations of the coordinated alkyne ligands in these and related complexes is under active investigation.

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**Supplementary Material Available:** Tables of crystal data, positional and thermal parameters, bond lengths, bond angles, and torsion angles for 1 and additional drawings of 1 (12 pages); a listing of calculated and observed structure factors for 1 (14 pages). Ordering information is given on any current masthead page.

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# Characterization of Rhodium Olefin Complexes Chemisorbed onto $\gamma$-Alumina by Solid-State $^{13}C$ NMR and EXAFS Spectroscopies

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*Summary:* Rhodium olefin and carbonyl complexes $[RhClL]_2$ (L = 1,5-cyclooctadiene (cod), $(C_2H_4)_2$, $(CO)_2$), chemisorbed onto partially dehydroxylated $\gamma$-alumina, are characterized by solid-state NMR and extended X-ray absorption fine structure (EXAFS) spectroscopies. $^{13}C$ NMR data indicate that the olefin ligands observed in the immobilized species remain bound to the rhodium centers. EXAFS studies reveal a ligand-dependent, reversible disruption of the Rh–Cl bonds upon chemisorption.

The manner in which transition metal-based catalysts are bound to support materials is of fundamental interest in the field of heterogeneous catalysis.[1] For many systems metal-support interactions are known to play important roles in their overall reactivity.[2] Unfortunately, the interactions between functional groups on the surface of a support and single metal atoms or aggregate assemblies remain obscure.[3] In this regard solid-state NMR methods utilizing cross polarization and magic angle spinning (CPMAS)[4] and EXAFS[5] spectroscopy have emerged as two important techniques capable of providing new and detailed information about surface-bound species in amorphous materials.[6,7]

Supported rhodium catalysts have been studied extensively due to the number of economically important pro-

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**Table I.** $^{13}C$ **CPMAS Data for the Neat and Chemisorbed Rhodium Species**

| | $^{13}C$ chem shifts/ppm | | | width of peak envelope$^e$/ppm | |
|---|---|---|---|---|---|
| complex | solution | neat solid$^d$ | chemisorbed$^d$ | neat solid | chemisorbed |
| 1 ($C_\alpha$) | 61.16$^c$ | 63.37 | 56.0 | 13.6 | 12.8 |
| 2 ($C_\alpha$) | 78.53$^{a,b}$ | 79.30 | 76.6 | 10.4 | 9.0 |
| | 78.80 | 80.15 | | | |
| | | 82.38 | | | |
| 2 ($C_\beta$) | 30.87$^a$ | 32.07 | 31.2 | 9.2 | 4.9 |
| | | 33.37 | | | |

$^a$ $CDCl_3$. $^b$ $J(^{13}C\text{-}Rh) = 13.8$ Hz. $^c$ $C_6D_6$. $^d$ Hexamethylbenzene was used as chemical shift reference with $\delta$(C(methyl)) = 17.36 ppm.[26] $^e$ Width of the peak envelope at the baseline; FID was processed with a line-broadening factor of 10 Hz. $^{13}C$ resonance frequency: 50.31 MHz.

cesses with which they are involved.[8] Most methods used to prepare highly dispersed rhodium on oxide-based supports involve a sequence of steps wherein changes in both the oxidation state and aggregation of the rhodium centers are involved.[7a–d] Schwartz and co-workers[9] have also described the adsorption and reactivity of the rhodium species that result when tris(allyl)rhodium is exposed to various oxide surfaces. In the study described here, preformed, dinuclear, chloro-bridged rhodium(I) olefin and carbonyl complexes are chemisorbed directly onto the surface of partially dehydroxylated alumina. Through EXAFS, solid-state $^{13}C$ NMR spectroscopy, and reactivity studies, we have characterized the rhodium species which result in the chemisorption process. We find that, in contrast to previously described systems,[7a–d] adsorption of a chloro-bridged dicarbonyl complex gives rise to surface-bound, mononuclear species which retain some of the Rh–Cl bonds present in the precursor. Furthermore, we have observed the ligand-dependent, reversible disruption of the Rh–Cl bonds upon chemisorption.

Partially dehydroxylated $\gamma$-alumina (PDA)[10] readily adsorbs chloro-bridged rhodium olefin and carbonyl complexes $[RhClL]_2$ from dichloromethane solutions.[11] Reproducible, maximum loadings of approximately 2% (wt) were obtained for the two olefin complexes. The carbonyl complex 3 is adsorbed more strongly, giving maximal loadings of approximately 4%.

(1)

$L_n = (C_2H_4)_2$ 1 1a
= cod 2 2a
= $(CO)_2$ 3 3a

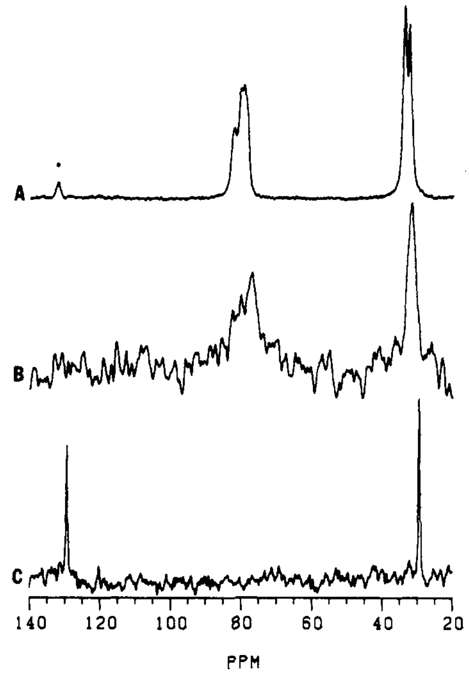

**Figure 1.** Solid-state $^{13}C$ NMR spectra of (A) 2 (800 scans), (B) 2a (23 000 scans), and (C) physisorbed cod (9000 scans). Conditions: spinning rate 4–5 kHz; contact time 1–3 ms, recycle time 3–4 s; line-broadening factors 10 Hz (A), 40 Hz (B), 20 Hz (C). The signal for added hexamethylbenzene reference is marked with an asterisk in A.

Carbon-13 chemical shift data in NMR spectra are quite sensitive to the nature and extent of interaction between a transition metal and an olefin.[12] Table I summarizes the chemical shift and line width parameters for the adsorbed cod and bis(ethylene) species 1a and 2a and for 1 and 2 as neat solids. Figure 1A,B compares the spectra obtained for the neat and the chemisorbed cod samples.

The chemical shifts of the olefinic and aliphatic carbons for solution, neat solid, and chemisorbed samples of 1 and 2 are all similar and quite distinct from the corresponding signals (129.3, 29.3 ppm) for physisorbed olefin (Figure 1C).[13] As a neat solid, the cod complex 2 gives rise to a spectrum having two groups of signals roughly centered about the chemical shift values observed for the carbons of 2 in solution. A total of five peaks of unequal intensities are discernible within the envelopes of the olefinic and aliphatic signals. We have determined the crystal structure[14] of 2 and found that the two cod ligands in the single unique molecule are coordinated asymmetrically to the rhodium atoms. Thus, in the solid state, the $sp^2$ and $sp^3$ carbons of these ligands can give rise to as many as eight independent signals. As shown in Figure 1A, only three olefinic and two aliphatic carbon signals are resolved for the neat complex in the solid state.

A single, broad signal centered at 63.4 ppm (envelope width 13.6 ppm) is observed for the ethylene ligands of 1 in the solid state. In solution, the ethylene ligands of 1 are known to exhibit intramolecular dynamic behavior and also give rise to a broadened NMR signal.[15] The X-ray

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[10] Majors, P. D.; Raidy, T. E.; Ellis, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 8123.

[11] Chemisorbed samples were washed extensively with dichloromethane to remove physisorbed materials.

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[13] Physisorbed cyclooctadiene was prepared by exposing an alumina slurry ($CH_2Cl_2$) to cod, followed by filtration and drying *briefly* under vacuum. Washing physisorbed samples caused the $^{13}C$ NMR signals for cod to disappear.

[14] (a) An early description of the structure 2[14b,c] has the inner, four-membered $Rh_2Cl_2$ ring planar within the limits of the model and the outer cod ligands coordinated symmetrically to each rhodium about this plane. We have redetermined the structure of 2 and found the puckering angle between the two Cl–Rh–Cl planes is 169.0°. Details of the structure will appear in a future publication. (b) Ibers, J. A.; Snyder, R. G. *Acta Crystallogr.* **1962**, *15*, 923. (c) Ibers, J. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 495.

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**Table II. XRD$^a$ and EXAFS Atom Separations**

| | D(Rh-Cl)/Å | | D(Rh-C$_\alpha$)/Å | |
|---|---|---|---|---|
| complex | XRD | EXAFS | XRD | EXAFS |
| $1^b$ | 2.39 | 2.39 | 2.12 | 2.08 |
| $2^{b,c}$ | 2.40 | 2.42 | 2.10 | 2.08 |
| $3^d$ | 2.38 | 2.39 | 1.85 | 1.81 |

$^a$ Mean atom separations; maximum range around the mean for any distance is ±0.03 Å. $^b$ Unpublished results. $^c$ Reference 14a. $^d$ Reference 17b.

structure of **1** in the solid state shows that the $Rh_2Cl_2$ ring is puckered,[16] similar to what is observed for the chloro-bridged dicarbonyl species **3**.[17] Puckering of such a four-membered ring produces endo and exo environments for the two ends of the coordinated ethylene ligands, which leads to the prediction of at least two different signals for the ethylene carbons. Rotation about the Rh–ethylene bond axis would average these two chemical environments.[18]

The spectra of the chemisorbed samples (**1a**, **2a**) are quite similar to those observed for **1** and **2**. Although the fine structure described for **2** is lost upon chemisorption, the chemical shift envelopes for the olefinic and aliphatic carbons of **1** and **2** are largely unaffected. Thus, chemisorption of these olefins complexes does not produce a significantly wider range of chemical shift environments for the organic ligands. No evidence for any other types of carbon is observed for any of these samples.

When a suspension of the adsorbed ethylene species **1a** on alumina is exposed to cyclooctadiene, the signal at 56 ppm is replaced by two signals which have chemical shifts identical to those observed for the directly adsorbed cod species, **2a**. When **1a** is exposed to carbon monoxide, the signal at 56 ppm is lost and two strong IR bands at 2097 and 2017 cm$^{-1}$ appear, consistent with the presence of a rhodium(I) *gem*-dicarbonyl species, $Rh(CO)_2$, on the surface.[19] These data, together with the chemical shift correlations, indicate that chemisorption of chloro-bridged olefin complexes gives rise to surface-bound species in which *all* of the olefin or carbonyl ligands are bound to rhodium.[20] Furthermore, olefin exchange reactions which are normally observed for the precursor complexes are not affected significantly by the chemisorption process.

While NMR spectroscopy provides information concerning the carbon in these samples, EXAFS is sensitive to the local environment about the rhodium. EXAFS data provide three types of information about the coordination environment of the rhodium: (1) Rh-to-scatterer distances; (2) scatterer identities (atomic number); (3) the number of scatterers of any particular type. The distance and identity information in these data is by far the most reliable and is directly comparable to X-ray diffraction (XRD) data obtained for the precursor complexes.

EXAFS spectra were collected at room temperature for the complexes **1**–**3** and for the corresponding adsorbed samples **1a**–**3a** (Figure 2, Table II).[21] In general, the EXAFS data for the neat complexes are in very good agreement with XRD studies on these complexes. For **1**–**3**, clear Rh–C and Rh–Cl features were observed in the Fourier transforms of the EXAFS data (e.g. the peaks at 1.6 and 2.0 Å in Figure 2A). Quantitative curve fitting of the first-shell EXAFS data[22] gives results in excellent agreement with the crystallographically determined structures (Table II). A variety of outer-shell features were also clearly evident in the EXAFS. Weak, temperature-dependent[23] Rh–Rh features were observed for all of the neat samples, while a weak Rh–C$_\beta$ for **2** and a strong Rh–O feature from the linear Rh–CO unit for **3** were also observed. No quantitative analysis was attempted for these outer-shell EXAFS features.

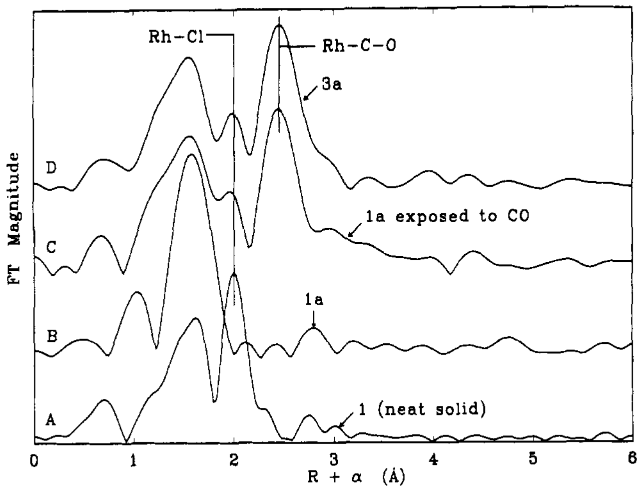

**Figure 2.** Offset plots of the Fourier transformed EXAFS data vs $R + \alpha$ for (A) **1**, (B), **1a**, (C) **1a** + CO, and (D) **3a**. Peaks shown here are shifted ca. 0.4 Å relative to the true atom separations (Table II and text) due to the EXAFS phase shift ($\alpha$).

The EXAFS data for the adsorbed species are quite different from those collected for the neat complexes.[24] The adsorbed olefin species, **1a** and **2a**, show no sign whatsoever of a Rh–Cl feature. The single, prominent feature for **1a** and **2a** can be modeled as Rh–O, Rh–C, or a combination of the two, with an average R–(C,O) distance of ca. 2.1 Å and an apparent coordination number of ca. 5. The lack of detectable Rh–Cl scattering indicates either that the Rh–Cl bonds are broken upon adsorption or significantly altered (e.g. enhanced static or dynamic disorder). Although these possibilities cannot be distinguished with the present data, we favor loss of Rh–Cl bonds, since this is most consistent with the observed increase in low-*Z* scattering at ca. 2.1 Å. The increase in Rh–(C,O) coordination number suggests that Rh–Cl bonds have been replaced by Rh–O interactions with the surface. In contrast, the EXAFS spectrum of the adsorbed carbonyl species **3a** shows a Rh–Cl feature as well as the expected

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(16) (a) Bateman, L. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 7292, footnote 38. (b) Unpublished results (C.E.B.).

(17) (a) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761. (b) Walz, L.; Scheer, P. *Acta Crystallogr.* **1991**, *C47*, 640.

(18) Further investigations of the dynamic behavior of the ethylene ligands of **1** in the solid state are underway.

(19) (a) Yates, J. T.; Kolasinski, K. *J. Chem. Phys.* **1983**, *79*, 1026. (b) Yates, J. T.; Haller, G. L. *J. Am. Chem. Soc.* **1984**, *88*, 4660. (c) Beebe, T. P.; Albert, M. R.; Yates, J. T. *J. Catal.* **1985**, *96*, 1.

(20) We are investigating the question of whether some rhodium centers lose their olefin or carbonyl ligands upon chemisorption. Preliminary, quantitative solid-state $^{13}C$ NMR studies indicate that there is little, if any, loss of cod from **2** upon chemisorption.

(21) Spectra were measured at SSRL wiggler beam line 7-3 under dedicated conditions (3.0 GeV, 50 mA). All measurements were made in transmission mode. Adsorbed samples were packed anaerobically in sealed cells; neat materials were diluted with BN prior to packing.

(22) Data were fit with empirical amplitude and phase parameters. EXAFS data for $K_3RhCl_3{\cdot}H_2O$, $Rh(H_2O)_6(ClO_4)_3$, and $[RhCl(cod)]_2$ (measured at 10 K) were used for Rh–Cl, Rh–O, and Rh–C interactions, respectively.

(23) Low-temperature (10 K) EXAFS data for these complexes show both the Rh–Cl and Rh–Rh features much more prominently than at room temperature, while the Rh–C and Rh–O features of the ethylene, cod, and CO ligands show little change with temperature. The temperature dependence of the EXAFS spectra for these complexes and the adsorbed species will be described in a full paper to follow this communication.

(24) Near-edge spectra for the neat and adsorbed materials are all very similar, thus ruling out changes in the rhodium oxidation state during adsorption.

Rh-O and Rh-C features for the Rh-carbonyl ligands. Thus, it appears that, in the adsorption process, most if not all of the Rh-Cl bonds are lost for the olefin complexes, while some are retained in the case of the carbonyl species.[25]

The most interesting observation in the EXAFS data is seen in the ethylene sample **1a** which has been exposed to carbon monoxide. The resulting sample gives rise to an EXAFS spectrum (Figure 2C) which is virtually identical to that for the CO complex adsorbed directly, **3a** (Figure 2D)—*including the Rh-Cl feature missing in the original ethylene sample.* The exchange reaction involves not only the quantitative replacement of the ethylene ligands bound to the Rh center but also re-formation of at least some of the Rh-Cl bonds which were lost in the initial adsorption process. The reversible disruption of the Rh-Cl bonds upon chemisorption can be rationalized in terms of the relative $\pi$-acid characteristics of the carbonyl and ethylene ligands. Chloride is a stronger $\pi$-base than the oxygen-based functionality found on the surface. Consequently, with carbonyl ligands, some Rh-Cl bonds remain upon chemisorption whereas all Rh-Cl bonds break when the ligands are either ethylene or cod. The fact that the disruption of the Rh-Cl bond is reversible indicates that the chloride from a broken Rh-Cl bond remains in close proximity to the rhodium atom and is available for bonding as soon as the $\pi$-acidity of the terminal ligand favors it over the competing oxide.

The present results differ from previously described systems in two important aspects. Other procedures for producing highly dispersed rhodium give rise to oxide-bound rhodium centers,[7] and little is known about the influence of ancillary ligands on metal-surface interactions. We have shown here that a different starting material and adsorption procedure gives rise to a significant number of the immobilized $Rh(CO)_2$ centers which have chloride as a directly bound ligand. Second, changes in the relative donor-acceptor abilities of the organic ligands can cause changes in metal support interactions. Specifically, chloride is reintroduced into the rhodium coordination sphere when the $\pi$-acid character of the organic ligand increases. Studies to determine the effects of other ligands such as phosphines and phosphites on the surface interactions between rhodium and alumina are in progress.

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(25) The presence of a small population of dinuclear clusters in the adsorbed samples is difficult to exclude, since the Rh-Rh EXAFS is weak at room temperature and, in the case of **3a**, is perturbed by the Rh-O EXAFS. Cryogenic measurements designed to address this question are in progress.

(26) Earl, W. L.; Vanderhart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.

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# *Articles*

## The Concept of Geometrical Rigidity around a Transition-Metal Center, a Significant Factor in Improving Thermal Stability for $\sigma$-Alkyl Transition-Metal Complexes

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*Received February 26, 1991*

Some four-membered cyclic ($\sigma$-alkylamino)palladium complexes containing conformationally free $\beta$-hydrogens have been prepared and show a thermal stability that seems hard to explain in traditional terms. However, their relative stabilities correlate with the extent that geometrical rigidity around the metal center is maintained by the ligands. This concept of geometrical rigidity around the metal center is also suggested to be effective as a stabilizing factor for some representative $\sigma$-alkyl transition-metal complexes extracted from the literature. At 20 °C the ($\sigma$-alkyl)palladium complexes undergo a slow $\beta$-hydride elimination and a reinsertion to afford five-membered palladacycles. Attempts to prepare acyclic $\sigma$-alkyl complexes from the four-membered cyclic palladium compounds by treatment with trifluoroacetic acid led to decomposition and the formation in good yield of 3-(*N*,*N*-dimethylamino)-1-butene, the expected product from a regioselective $\beta$-hydride elimination.

### Introduction

Transition-metal-catalyzed reactions frequently involve $\sigma$-alkyl intermediates. In most cases the chemistry of these $\sigma$-alkyl intermediates constitutes the scope and limitation of the catalysis. This crucial dependence of $\sigma$-alkyl complex chemistry is apparent in a wide range of catalytic reactions spanning from strategic scale operations such as polymerization of alkenes down to laboratory scale cross-coupling reactions between alkyl main-group metals and, for example, organic halides (vide infra). A better understanding of the chemistry of $\sigma$-alkyl transition-metal complexes is therefore frequently linked to a better un-