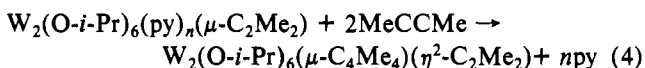
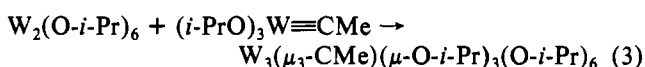
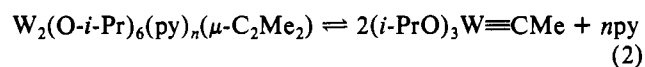
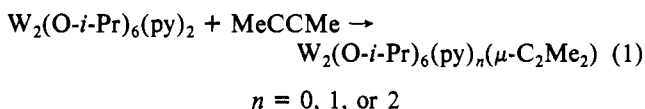


pyramidal units are fused together through the agency of a  $\mu_3$ -CMe ligand and by three basal  $\mu$ -OR ligands. The 360-MHz  $^1\text{H}$  NMR spectrum recorded in toluene- $d_8$  at  $-1^\circ\text{C}$  is as expected on the basis of the solid-state structure. Specifically there are two types of O-*i*-Pr ligands in the ratio of 1:2 assignable to bridging and terminal groups, respectively, and the latter, but not the former, show diastereotopic methyl groups.<sup>12</sup> The signal assignable to the  $\mu_3$ -CMe protons shows coupling to  $^{183}\text{W}$  ( $I = 1/2$ , natural abundance 14.3%), and the satellite intensities are consistent with expectations for a triply bridging group (31.5% of the total signal intensity is due to the isotopomer containing one  $^{183}\text{W}$  nucleus).

The W-W distances, 2.75 Å, are notably longer than those seen in  $\text{M}_3(\mu_3\text{-O})(\mu_3\text{-O-}i\text{-Pr})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$  compounds ( $\text{M-M} = 2.53 \text{ \AA}$  ( $\text{M} = \text{Mo}$ ) and  $2.54 \text{ \AA}$  ( $\text{M} = \text{W}$ )).<sup>13,14</sup> The present structure may be viewed formally as a derivative of the  $\text{M}_3(\mu_3\text{-O})(\mu\text{-O})_3^{4+}$  structure in which one of the octahedral sites, that trans to the capping ligand, is vacant.

Of interest, too, is how the new compound is formed in the reaction between  $\text{W}_2(\text{O-}i\text{-Pr})_6$  and  $\text{MeC}\equiv\text{CMe}$ . We believe that all the products can be accounted for in terms of reactions 1-4.



Reaction 1 has parallels in the synthesis of other alkyne adducts of ditungsten hexaalkoxides.<sup>6,7</sup> The equilibrium (2) has been found<sup>7</sup> for  $\text{W}_2(\text{O-}t\text{-Bu})_6(\mu\text{-C}_2\text{H}_2)(\text{py})$  and  $(t\text{-BuO})_3\text{W}\equiv\text{CH}$ , and dialkylacetylenes are known to react with  $\text{W}_2(\text{O-}t\text{-Bu})_6$  to give  $(t\text{-BuO})_3\text{W}\equiv\text{CR}$  compounds.<sup>15</sup> The comproportionation reaction (3) has a direct analogy to the synthesis of  $\text{M}_3\text{O}(\text{O-}i\text{-Pr})_{10}$  clusters from  $\text{MO}(\text{O-}i\text{-Pr})_4$  and  $\text{M}_2(\text{O-}i\text{-Pr})_6$  compounds<sup>13,14</sup> and is similar to (1). The coupling of the alkyne units in (4) is also now well documented.<sup>10,16</sup>

If the proposed reaction sequence is correct, it should be possible to synthesize an extensive class of related compounds including perhaps  $\mu$ -nitrido clusters by the comproportionation of  $\text{M}\equiv\text{N-}$  and  $\text{M}\equiv\text{M}$ -containing compounds. Further studies are in progress.<sup>17</sup>

**Registry No.**  $\text{W}_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$ , 92054-28-9;  $\text{W}_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_4\text{Me}_4)(\eta^2\text{-C}_2\text{Me}_2)$ , 87654-13-5;  $\text{W}_2(\text{O-}i\text{-Pr})_6(\text{py})_2$ , 70178-75-5;  $\text{MeC}\equiv\text{CMe}$ , 503-17-3.

**Supplementary Material Available:** Listing of fractional coordinates and isotropic thermal parameters (1 page). Ordering information

is given on any current masthead page.

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## Olefin Coordination with Rhodium(II) Trifluoroacetate

Sir:

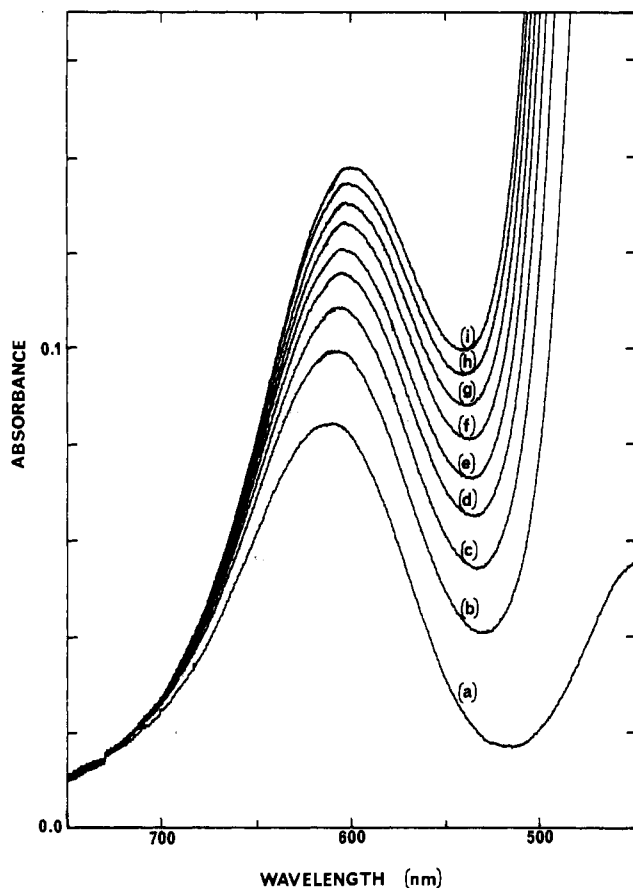
Rhodium(II) carboxylates are being employed with increasing frequency as catalysts for carbenoid reactions of diazo compounds with unsaturated substrates,<sup>1,2</sup> for olefin hydrogenation,<sup>3</sup> and for autooxidation of alkenes.<sup>4</sup> Extensive structural information is available for these diamagnetic complexes that possess one coordination site per metal,<sup>5</sup> and their formation of 1:1 and 1:2 adducts with Lewis bases is well documented. Recently, Drago and co-workers have concluded that the filled, essentially  $\pi^*$  orbitals of rhodium(II) carboxylates are very effective at  $\pi$  back-donation into  $\pi$ -acceptor ligands.<sup>6,7</sup> However, complexes with olefins have not been observed, and rhodium(II) carboxylates are generally regarded as incapable of such coordination.<sup>8</sup>

We now report the first demonstration of olefin coordination with a rhodium(II) carboxylate and equilibrium constants for the 1:1 adducts of  $\text{Rh}_2(\text{OOC}\text{CF}_3)_4$  with a representative series of alkenes. Sequential addition of aliquots of 2,5-dimethyl-2,4-hexadiene to  $\text{Rh}_2(\text{OOC}\text{CF}_3)_4$  in anhydrous dichloromethane under nitrogen produces the spectral changes described in Figure 1. A spectral shift from the initial  $\lambda_{\text{max}}$  of 610 nm to a limiting value of 590 nm is observed. A plot of  $1/\Delta A$  vs.  $1/[\text{diene}]$  and/or  $\Delta A$  vs.  $\Delta A/[\text{diene}]$ <sup>9</sup> shows a linear correlation (correlation coefficient  $>0.99$ ) that describes a 1:1 complex between  $\text{Rh}_2(\text{OOC}\text{CF}_3)_4$  and 2,5-dimethyl-2,4-hexadiene. Results obtained with concentrations of  $\text{Rh}_2(\text{OOC}\text{CF}_3)_4$  only half that reported in Figure 1 confirm this interpretation. In contrast, the absorption spectrum of  $\text{Rh}_2(\text{OOC}\text{CCH}_3)_4$  is unaffected by 2,5-dimethyl-2,4-hexadiene or any other olefin employed in this investigation.

Table I reports equilibrium constants for adduct formation of a representative series of olefins with  $\text{Rh}_2(\text{OOC}\text{CF}_3)_4$ . Equilibrium constants were calculated from absorbance/concentration data by the procedure previously described for 2,5-dimethyl-2,4-hexadiene. A minimum of two separate determinations was made for each olefin, and  $K_{\text{eq}}$  values were reproducible to within  $\pm 7\%$ . Comparison of  $K_{\text{eq}}$  values in Table I for 1-hexene, *trans*-3-hexene or *trans*-4-octene, and 2-methyl-2-butene shows that increasing alkyl substitution of the carbon-carbon double bond favors coordination. Complex formation with *trans* olefins is favored over that with cyclohexene, and vinyl ethers form the strongest adducts. Qualitatively, these results are consistent with  $\pi$ -donor stabilization

- (12)  $^1\text{H}$  NMR data from a toluene- $d_8$  solution at  $-1^\circ\text{C}$  (360 MHz):  $\delta = 4.99$ , septet,  $J_{\text{HH}} = 6 \text{ Hz}$  (6 H);  $\delta = 4.12$ ,  $J_{\text{WH}} = 6.9 \text{ Hz}$  (3 H);  $\delta = 3.64$ , septet,  $J_{\text{HH}} = 6 \text{ Hz}$  (3 H);  $\delta = 1.47$ , doublet,  $J_{\text{HH}} = 6 \text{ Hz}$  (18 H);  $\delta = 1.41$ , doublet,  $J_{\text{HH}} = 6 \text{ Hz}$  (18 H);  $\delta = 1.26$ , doublet,  $J_{\text{HH}} = 6 \text{ Hz}$  (18 H).  $\delta$  is relative to  $\text{Me}_4\text{Si}$ .
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**Figure 1.** Visible spectral changes accompanying sequential additions of 2,5-dimethyl-2,4-hexadiene to  $\text{Rh}_2(\text{OOCCF}_3)_4$  ( $4.00 \times 10^{-4}$  M) in dichloromethane at 25 °C.  $[\text{Me}_2\text{C}=\text{CHCH}=\text{CMe}_2]$  ( $10^3$  M): (a) 0; (b) 2.34; (c) 4.67; (d) 6.99; (e) 9.35; (f) 11.7; (g) 14.0; (h) 16.4; (i) 18.7.

**Table I.** Equilibrium Constants for Olefin Coordination with  $\text{Rh}_2(\text{OOCCF}_3)_4$  in Dichloromethane at 25 °C<sup>a</sup>

olefin	$K_{\text{eq}}$	olefin	$K_{\text{eq}}$
styrene	6.1	2-methyl-2-butene	133
1-hexene	42	<i>n</i> -butyl vinyl ether	135
cyclohexene	42	dihydropyran	170
<i>trans</i> -3-hexene	66	ethyl vinyl ether	224
<i>trans</i> -4-octene	68	2-methoxypropene	578
2,5-dimethyl-2,4-hexadiene	128		

<sup>a</sup>  $[\text{Rh}_2(\text{OOCCF}_3)_4]_1 = 4.00 \times 10^{-4}$  M.

of the increased partial positive charge on the metal in  $\text{Rh}_2(\text{OOCCF}_3)_4$ .<sup>7</sup> Neither  $\alpha,\beta$ -unsaturated carbonyl compounds such as 3-buten-2-one nor the three diphenylethylenes exhibits detectable interaction with  $\text{Rh}_2(\text{OOCCF}_3)_4$ . Only 1:1 adducts with limiting  $\lambda_{\text{max}}$  of  $586 \pm 6$  nm were detectable when complex formation could be observed.

As indicated by the visible spectrum of the rhodium(II) adduct of 2,5-dimethyl-2,4-hexadiene (Figure 1), these complexes do not exhibit the electronic characteristics previously observed with Lewis bases.<sup>6,7</sup> However, benzene complexes

of rhodium(II) butyrate, previously proposed to account for thermodynamic differences in adduct formation with Lewis bases in benzene and methylene chloride solutions,<sup>10</sup> exhibit similar spectral characteristics. The present study is consistent with that interpretation, although the nature of the metal association with these  $\pi$  donors requires further investigation.

Additional support for these olefin complexes was obtained from NMR spectroscopy where the chemical shifts of olefin protons were observed to increase uniformly with the molar ratio of  $\text{Rh}_2(\text{OOCCF}_3)_4$  to olefin.<sup>11</sup> For example, the time-averaged chemical shift of the vinyl proton of 2-methyl-2-butene increased linearly from  $\delta$  5.2 ( $[\text{Rh}_2(\text{OOCCF}_3)_4]/[\text{olefin}] = 0$ ) to  $\delta$  6.3 ( $[\text{Rh}_2(\text{OOCCF}_3)_4]/[\text{olefin}] = 0.33$ ), and smaller increases in chemical shift ( $\delta < 0.2$ ) were observed for methyl protons. Similar results were obtained for 2,5-dimethyl-2,4-hexadiene and 2-methoxypropene, but the limited solubility of  $\text{Rh}_2(\text{OOCCF}_3)_4$  in chloroform-*d* at low olefin concentrations prevented accurate determination of the chemical shifts of the coordinated olefin for any of these complexes. These data suggest the effectiveness of rhodium(II) perfluorocarboxylates as olefin-specific NMR shift reagents, and this utilization is currently under investigation.

Association constants for olefin complexes with rhodium(II) trifluoroacetate do not correlate with those for olefin complexes with Rh(I), Pd(II), Pt(II), or Ag(I)<sup>11</sup> where  $\pi$  back-bonding has a dominant influence on complex stability. Instead, the ability of  $\text{Rh}_2(\text{OOCCF}_3)_4$  to coordinate with olefins results from the increased covalent and electrostatic  $\sigma$ -acceptor properties of the trifluoroacetate ligand. Relative to  $\text{Rh}_2(\text{OAc})_4$ , which is not observed to coordinate with olefins,  $\text{Rh}_2(\text{OOCCF}_3)_4$  has a decreased tendency for metal-to-ligand back-bonding.<sup>7</sup> Complex formation is remarkably sensitive to the  $\sigma$ -donor capability of olefin substituents, and as can be seen from the data in Table I, association constants are relatively insensitive to steric influences. Qualitatively, these association constants correlate with olefin ionization potentials,<sup>12</sup> which are closely related to HOMO energies. That only 1:1 complexes of  $\text{Rh}_2(\text{OOCCF}_3)_4$  with olefins are detected is consistent with the greatly decreased acceptor capability of 1:1 rhodium(II) complexes.<sup>7,10</sup>

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**Registry No.**  $\text{Rh}_2(\text{OOCCF}_3)_4$ , 31126-95-1.

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