highly symmetrical reaction coordinate; however, the exact values are not known with certainty because of the departure from the rule of the geometric mean. Despite the symmetry of the reaction coordinate, no direct evidence for tunneling was obtained. However, the criteria used to assess the role of tunneling may be excessively rigid.[4] Further studies are needed to clarify the apparent partial failure of the RGM. It may be that the deviation results from an unrecognized source of error in the measurements or that it is in fact an unexplained but real physical phenomenon.

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Communications to the Editor

Formation of Metallocycloimides from the Reaction of Isocyanates with a Neutral Transition-Metal Carbonyl

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We recently reported that the activation of CO_2 by η^1-C complexation to $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ results in facile oxygen exchange between coordinated CO_2 and coordinated CO, and we suggested that these exchanges follow attack by a nucleophilic oxygen of the CO_2 ligand on a neighboring carbonyl ligand.[1] The transient metalloanhydride proposed is analogous to the metalloheterocycles which Fehlhammer has reported as major or minor products of the reactions of $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ with heteroallenes such as carbodiimides,[2] isothiocyanates,[3] and ketenimines.[4] The facility of the oxide transfer in this anionic system suggested that metalloanhydrides and other heteroallene adducts might also be formed by carbonyl complexes which are neutral but electron rich,[5] and we now wish to report the syntheses of the first metallocycloimide complexes by addition of isocyanates to a neutral carbonyl complex.

Oxidative addition of methyl iodide[6] to $[W(\eta\text{-}C_5H_5)_2(CO)]$[7] (**1**) indicates that **1** is an exceptionally nucleophilic neutral carbonyl complex and a promising substrate for the addition of heteroallenes. Addition of methyl isocyanate (13.0 mL, 220 mmol) to an intensely green slurry of $[W(\eta\text{-}C_5H_5)_2(CO)]$ (0.648, g, 1.90 mmol) in pentane (60 mL) led over 1 h to formation of an orange solution and a bright orange precipitate. The supernatant was decanted off and the powder washed with pentane and vacuum dried to give 0.667 g (1.67 mmol ≡ 87%) of spectroscopically pure $[W(\eta\text{-}C_5H_5)_2[\overline{C(O)N(CH_3)C(O)}]]$ (**2**). Analytically pure **2** was obtained as irregular needles (ca. 90% recovery) from acetone at −78 °C.[8]

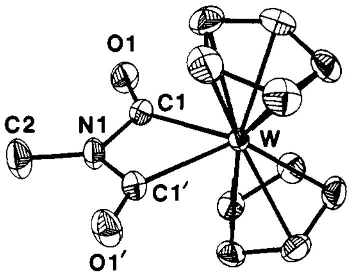

Figure 1. Molecular structure of $[W(\eta\text{-}C_5H_5)_2[\overline{C(O)N(CH_3)C(O)}]]$ (50% probability ellipsoids). Primed atoms are symmetry generated by the plane through the W and N atoms perpendicular to the metallocycloimide plane. Selected bond lengths (Å) and angles (deg): W–C(1) = 2.195 (3), C(1)–O(1) = 1.213 (5), C(1)–N(1) = 1.393 (4), N(1)–C(2) = 1.451 (7); C(1)–W–C(1′) = 60.3 (2), W–C(1)–N(1) = 97.4 (2), C(1)–N(1)–C(1′) = 104.7 (4), C(1)–N(1)–C(2) = 127.5 (2), W–C(1)–O(1) = 139.4 (3).

The metallocycloimide structure of **2** (Figure 1) was established by an X-ray diffraction study of the orange cubes obtained by cooling a saturated acetone solution to 0 °C over a 4-h period.[9] The metallocycle core of the molecule is reminiscent of the structures of typical cyclic imides,[11] and the metal atom, the ring carbon atoms, and the nitrogen atom are essentially coplanar. The planar geometry of the nitrogen atom,[12] and the short nitrogen-ring carbon bond lengths of 1.393 (4) Å, indicates that the nitrogen lone pair is delocalized over the carbonyl carbons.

Formation of metallocycloimides from **1** is not restricted to methyl isocyanate, and a slurry of **1** (0.284 g, 0.83 mmol) in pentane (30 mL) reacted immediately with excess PhNCO (2.0 mL, 18.3 mmol) to give a pale orange powder. After 1 h the

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(8) ^1H NMR (acetone-d_6, 300.13 MHz) δ 4.95 (s, 10, $2C_5H_5$), 2.31 (s, 3, NCH_3); ^{13}C NMR (Me_2SO-d_6, gated decoupled, 75.47 Mhz) δ 176.2 (s, satellites J_{W-C} = 93.4 Hz, C=O), 86.3 (d, J = 183 Hz, C_5H_5), 22.8 (q, J = 138 Hz, CH_3); mass spectrum (parent ion, ^{184}W), m/e 399. Anal. Calcd for $C_{13}H_{13}NO_2W$: C, 39.12; H, 3.29; N, 3.51. Found (Schwarzkopf Laboratories, NY; sample dried at 10^{-4} mmHg for 24 h to remove occluded H_2O): C, 39.06; H, 3.37; N, 3.58.

(9) The diffraction study revealed the presence of one molecule of water of crystallization per molecule of **2** (IR confirmed the presence of H_2O in a bulk sample of the orange cubes and its absence from analytical samples). Crystal data: monoclinic space group $P2_1/m$, $Z = 2$, a = 7.659 (2) Å, b = 8.672 (2) Å, c = 9.656 (2) Å, β = 101.45 (2)°, d_{calcd} = 2.20 g/cm^3, μ = 97.1 cm^{-1}, λ(Mo Kα) = 0.71069 Å. Of the 3158 reflections measured in the range $3° \le 2\vartheta \le 60°$ on a Nicolet R3 four-circle diffractometer, 1881 unique reflections with $I > 3\sigma$ were used in the structure solution (Patterson) and refinement (SHELXTL).[10] Least-squares refinement with a block-diagonalized matrix converged at R = 2.20% and R_w = 2.19%. The hydrogen atoms of the water molecule were not located, and all other hydrogen atoms were placed in calculated positions. The largest unassigned peak in the final difference map (0.88 e$^-$/Å$_3$) was located 0.91 Å from the oxygen atom of the water.

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(12) The nitrogen atom is only 0.041 Å above the plane defined by C(1), C(2), and C(1′).

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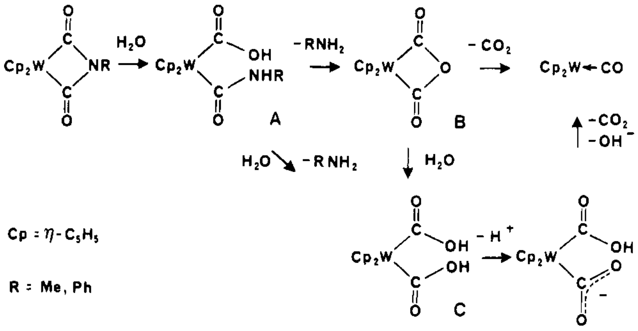
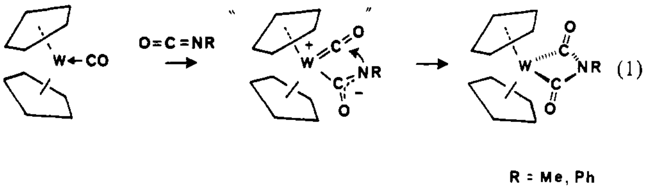
Scheme I. Possible Mechanisms for the Solvolysis of the Metallocycloimides **2** and **3** to the Carbonyl Complex **1**



supernatant was decanted off and the precipitate washed with pentane and vacuum dried to give 0.331 g (0.72 mmol ≡ 87%) of analytically pure $[\overline{W(\eta\text{-}C_5H_5)_2[C(O)N(Ph)C(O)}]]$ (**3**).[13]

The most reasonable mechanism for formation of **2** and **3** involves initial η^1-C coordination of a Lewis acidic isocyanate to the basic metal center (eq 1). In the zwitterionic intermediate



(1)

the heteroallene is nucleophilic at the β position and the carbonyl is electrophilic at the α position, and subsequent reaction gives a four-membered metalloheterocycle. Ring closure through nitrogen probably reflects the greater strength of C=O bonds as compared with C=N bonds: the isomeric metalloisoimide contains one C=O and one C=N bond in place of the two C=O bonds in **2** and **3**.[14]

Although metallocycloimides might be formed from many carbonyl substrates, we have discovered no other reports of metalloheterocycle formation from the reaction of isocyanates, nor any other heteroallene, with neutral carbonyl complexes. It is known, however, that carbonyls of the group 6 and 8 metals react with isocyanates to form isocyanide complexes,[15] and this reaction has been used as the first step in the catalytic conversion of isocyanates to carbodiimides and CO_2.[16] Both reactions probably proceed through metallocycloisoimides related to **2** and **3**, and metallocycloisoimides and metallocycloimides may be more accessible than previous reports imply.

Hydrolysis of the metallocycloimides is more facile than hydrolysis of cyclic organic imides[17] and does not require basic or acidic catalysis. A THF solution of the *N*-phenyl complex **3** reacts with a large excess of water to regenerate **1** in 1 day. The *N*-methyl complex **2** is less water sensitive than **3** (presumably because the N lone pair is in conjugation with the phenyl ring[17]), and **2** was inert to excess water in acetone at ambient temperatures for 1 day. It was, however, converted cleanly to **1** when the temperature was raised to 55 °C for 20 h. Hydrolysis of cyclic organic imides typically gives amidic acids,[17] and tungsten analogues of such species (A) are reasonable intermediate in the hydrolysis of **2** and **3** (Scheme I). The details of the conversion of A to **1** are unclear at this point, but some possibilities are shown.[18]

Attempts to extend the reaction of **1** with heteroallenes to the preparation of the metalloanhydride B have been unsuccessful. In toluene **1** was inert to 1.7 atm of CO_2 (65 equiv) up to 85 °C, and **1** recovered from a toluene solution after 3 h at 65 °C under 6.5 equiv of $^{13}CO_2$ at a pressure of ca. 0.14 atm did not contain ^{13}CO (MS and IR). We conclude that the exceptional stability of CO_2 precludes metalloanhydride formation by a sequence analogous to that in eq 1.

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Registry No. 1, 39333-44-3; **2**, 106865-69-4; **3**, 106880-55-1; MeNCO, 624-83-9; PhNCO, 103-71-9.

Supplementary Material Available: Figures showing atomic numbering scheme and packing within the unit cell; tables of atomic positional and thermal parameters, intramolecular bond lengths and angles, least squares planes, interplanar angles, and angles about tungsten (5 pages); tables of structure factors (11 pages). Ordering information is given on any current masthead page.

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(13) ^1H NMR (acetone-d_6, 300.13 MHz) δ 7.42–7.36, 7.26–7, 7.10–7.03 (m, 5, C_6H_5), 5.10 (s, 10, $2C_5H_5$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 0 °C, 75.47 MHz) δ 176.6 (s, satellites $J_{W-C} = 91.6$ Hz, C=O), 134.5 (s, C_6H_5), 128.6 (s, C_6H_5), 126.0 (s, C_6H_5), 123.7 (s, C_6H_5), 84.4 (s, C_5H_5). Anal. Calcd for $C_{18}H_{15}NO_2W$: C, 46.87; H, 3.28; N, 3.04. Found (Galbraith Laboratories, TN): C, 47.10; H, 3.30; N, 3.15.

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(18) The formation of aniline and CO_2 after partial hydrolysis of **3** was confirmed by ^1H NMR (aniline) and GC (CO_2) analysis of a sample in acetone-d_6.

Catalytic Antibodies

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Antibodies bind biological macromolecules as well as small synthetic molecules with enzymelike affinities and specificities.[1] Moreover, because antibodies can be generated selectively against almost any target molecules of interest, antibodies have become one of the most important classes of receptors in medicine and biology today.[2] The development of strategies for introducing catalytic activity into the combining sites of antibodies might therefore afford a general route to catalysts with *tailored specificities*. We[3] and others[4] recently reported that antibodies that bind phosphate and phosphonate tetrahedral transition-state analogues catalyzed the selective hydrolysis of carbonates or esters. We now report the rational generation of a catalytic antibody that selectively hydrolyzes a predefined substrate. The antibody-catalyzed hydrolytic reaction displays saturation kinetics and substrate specificity and is competitively inhibited by the corre-

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