nickel–ligand basal distances. Bond distance data[8] for high-spin nickel(II) square pyramid show slightly longer basal bonds relative to apical bonds, averaging a few hundredths of an angstrom longer.

While it is expected[13] that d^8 low-spin five-coordinated complexes follow the observed pattern for relative bond lengths in the two geometrical types, d^9 complexes should follow this pattern to a lesser degree, not to a greater degree as observed for copper(II). Possibly, the addition of an electron to the SP b_1 level, which is strongly metal–basal ligand antibonding, serves to lengthen the apical copper–ligand bond rather than to decrease the trans basal angle θ. This could occur if the $x^2 - y^2$ orbital mixes in an antibonding way with basal ligand orbitals for copper complexes and as a consequence results in a destabilization of the b_1 level and hydridization away from the basal ligands toward the apical site. With considerable basal π bonding for copper complexes enhancing bond electron pair repulsions, this would rationalize the high θ value maintained for square-pyramidal copper(II) complexes (Figure 7).

As a final point, both the θ distortion coordinates and the dihedral angle coordinates suggest that the concerted axial-equatorial bending process is a predominant feature in assessing molecular distortions for five-coordinated derivatives. Further, the ease of distortion along these coordinates, whether by relief of ligand ring strain, steric effects, particular electronic properties of ligands, or lattice effects, implies that they represent a basis for stereochemical nonrigidity prevalent in solution for some five-coordinated members. Although structures of transition-metal derivatives tend to concentrate more readily toward the square pyramid for many of the elements, particularly d^6 complexes, there is a distribution covering the range between the two idealized limits in most cases. The preference of low-spin d^6 complexes for the square pyramid is supported by both the angular overlap model[12] and the relative ordering of energy levels in Figure 8.[13]

Acknowledgment. The support of this research by the National Science Foundation (CHE 8205411) is greatly appreciated. I am extremely grateful to Professor Roberta O. Day and Joan M. Holmes, who carried out the calculations on structural distortions.

Anionic Group 6B Metal Carbonyls as Homogeneous Catalysts for Carbon Dioxide/Hydrogen Activation. The Production of Alkyl Formates

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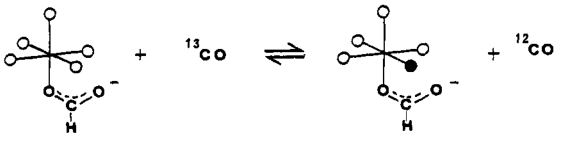
Abstract: The production of alkyl formates from the hydrocondensation of carbon dioxide in alcohols utilizing anionic group 6B carbonyl hydrides as catalysts is herein reported. $HM(CO)_5^-$ (M = Cr, W; derived from μ-$H[M_2(CO)_{10}]^-$) and their products of carbon dioxide insertion, $HCO_2M(CO)_5^-$, have been found to be effective catalysts for the hydrogenation of CO_2 in alcohols under rather mild conditions (loading pressures of CO_2 and H_2, 250 psi each, and 125 °C) to provide alkyl formates. The only metal carbonyl species detected in solution via infrared spectroscopy, both at the end of a catalytic period and during catalysis, were $M(CO)_6$ and $HCO_2M(CO)_5^-$. The metal hexacarbonyls were independently shown to be catalytically inactive. A catalytic cycle is proposed which initially involves release of formic acid from the metal center, either by reductive elimination of the hydrido formato ligands or ligand-assisted heterolytic splitting of dihydrogen with loss of formic acid. In a rapid subsequent process HCOOH reacts with alcohols to yield HCOOR. The addition of carbon monoxide retards alkyl formate production, strongly implying CO_2 to be the primary source of the carboxylic carbon atom in HCOOR. This was verified by carrying out reactions in the presence of $HCO_2W(^{13}CO)_5^-$ which provided *only* $H^{12}COOR$ after short reaction periods. However, in the *absence of hydrogen and carbon dioxide* μ-$H[M_2(CO)_{10}]^-$ species were observed to be effective catalyst precursors for converting CO and methanol into methyl formate.

The anionic metal carbonyl hydrides of the group 6B metals have been shown to reversibly bind carbon dioxide with concomitant formation of metalloformate derivatives (eq 1).[1-3] The

$$HM(CO)_5^- + CO_2 \rightleftharpoons HCO_2M(CO)_5^- \qquad (1)$$

forward reaction, i.e., the insertion of carbon dioxide into the metal–hydrogen bond, occurs instantaneously even at low pressures of carbon dioxide (<760 torr); however, the reverse process, decarboxylation, proceeds at ambient temperature only in the case where M = Cr.

On the other hand, the $HCO_2M(CO)_5^-$ species all undergo facile CO ligand substitution reactions with ^{13}CO, a process which occurs stereoselectively at the cis (equatorial) CO sites (eq 2). This is



(2)

in fact a feature common to a large variety of O-bonded metal entities,[4] and it is a process of importance in the decarboxylation pathway, i.e., excess carbon monoxide retards the extrusion of CO_2

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Table I. Synthesis of Methyl Formate by Catalytic Hydrogenation of Carbon Dioxide in Methanol[a]

expt	catalyst[b]	turnover no.[c]
1	$\mu\text{-H}[W_2(CO)_{10}]^-$	14.7[d]
2	$HCO_2W(CO)_5^-$	16.4[d]
3	$W(CO)_6$	–
4	$ClW(CO)_5^-$	1.6
5	$CH_3CO_2W(CO)_5^-$	15.1 (HCO_2CH_3)[d] 0.9 ($CH_3CO_2CH_3$)[d]
6	$\mu\text{-H}[W_2(CO)_{10}]^-$[e]	5.1
7	$HCO_2W(CO)_5^-$[e]	3.8
8	$\mu\text{-H}[Cr_2(CO)_{10}]^-$	14.5[d]
9	$HCO_2Cr(CO)_5^-$	14.6

[a] Temperature 125 °C and reaction time 24 h. [b] Catalyst concentrations were all 9.2×10^{-3} M, and the counterion was PPN = bis(triphenylphosphine)imminium. [c] Turnover = moles of HCO_2Me/moles of catalyst. [d] Duplicate runs carried out with similar results. Trace quantities of carbon monoxide were observed at the end of a catalytic run (0.05% of total gas composition as detected by GC). [e] Runs carried out in the presence of 100 psi (loading pressure) of carbon monoxide.

in these metalloformate derivatives.

Neutral group 6B metal complexes have been demonstrated to bind dihydrogen; e.g., $W[P(OMe)_3]_5H_2$[5] and $Mo(CO)_3[P\text{-}i\text{-}Pr_3]_2H_2$[6] have been well characterized. The latter species has been shown to possess an η^2-H_2 bonding mode by neutron diffraction. In addition, $M(CO)_6$ (M = Cr, Mo, W) compounds are good catalysts in the photoinduced hydrogenation of conjugated dienes.[7] Hence $HM(CO)_5^-$ complexes possess qualities which should make them good candidates as catalysts for hydrocondensation reactions of carbon dioxide; they readily insert carbon dioxide with metalloformate formation, and, subsequently, these formate derivatives undero facile CO ligand dissociation affording sites for dihydrogen binding.

This article reports the catalysis of reactions of CO_2 and molecular hydrogen by anionic group 6B metal–hydrides and –formates in the presence of alcohols to provide alkyl formates.[8,9] Organic derivatives in this class represent important industrial chemicals. For example, methyl formate readily serves as a chemical feedstock for a large variety of useful organic substances, some of these being formic acid, formamide, acetic acid, trichloromethyl chloroformate, and ethylene glycol.[10,11] In this regard special attention is being paid in our laboratories to obtaining a better understanding of the mechanism of methyl formate derived from carbon dioxide over a broad range of catalysts.[12]

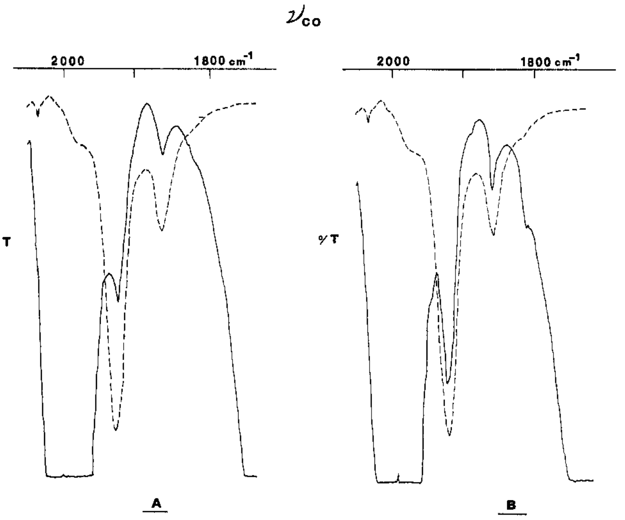

Figure 1. Infrared spectra in the ν(CO) region in methanol solvent. (A) After a 24-h catalytic period employing $\mu\text{-H}[W_2(CO)_{10}]^-$ as catalyst; (---) spectrum of pure $HCO_2W(CO)_5^-$. (B) After a 24-h catalytic period employing $HCO_2W(CO)_5^-$ as catalyst; (---) spectrum of pure $HCO_2W(CO)_5^-$.

Results and Discussion

The anionic group 6B carbonyl hydrides, $HM(CO)_5^-$ (M = Cr, W; derived from $\mu\text{-H}[M_2(CO)_{10}]^-$), and their products of carbon dioxide insertion, $HCO_2M(CO)_5^-$, have been found to be effective catalysts for the hydrogenation of CO_2 in methanol under rather mild conditions (loading pressures of CO_2 and H_2, 250 psi each, and 125 °C) to provide methyl formate (eq 3).[13] Table I contains reactivity data for these catalytic processes.

$$CO_2 + H_2 + ROH \xrightarrow{[\text{cat.}]} HCO_2R + H_2O \tag{3}$$

As indicated in Table I, both $\mu\text{-H}[M_2(CO)_{10}]^-$ and $HCO_2M(CO)_5^-$ display similar activities for methyl formate formation, with the latter being slightly more active. These results are understood in terms of the bridging hydride species undergoing heterolytic bond fission under the conditions of catalysis, hence providing a convenient source of $HM(CO)_5^-$. These latter derivatives have been demonstrated to rapidly add carbon dioxide to provide $HCO_2M(CO)_5^-$.[1-3] Activation parameters for the analogous heterolytic bond fission process involving the $\mu\text{-H}[Cr(CO)_5]_2^-$ species in 2-pentanol (eq 4) have been determined

$$\mu\text{-H}[Cr(CO)_5]_2^- \xrightarrow{\text{rds}} HCr(CO)_5^- + [Cr(CO)_5] \xrightarrow[\text{rapid}]{CO} 2Cr(CO)_6 + H_2 \tag{4}$$

to be $\Delta H^* = 93.3$ (4.6) kJ/mol and $\Delta S^* = -74.5$ (14.7) J/mol·deg.[14] The half-life for reaction 4 at 97 °C is approximately 1 h. It is worthy to note that both $\mu\text{-H}[M(CO)_5]_2^-$ and $HCO_2M(CO)_5^-$ complexes are more suitable catalysts than $HM(CO)_5^-$, since both of the former species are easily prepared and are more oxygen resistant than the mononuclear hydride derivatives.[15,16]

Subsequent to catalytic runs which used either $\mu\text{-H}[M(CO)_5]_2^-$ or $HCO_2M(CO)_5^-$ as catalyst, the only metal carbonyl species detected in solution via infrared spectroscopy were $M(CO)_6$ (major component) and $HCO_2M(CO)_5^-$ as depicted in Figure 1. This was confirmed by in situ FT infrared spectra taken during a

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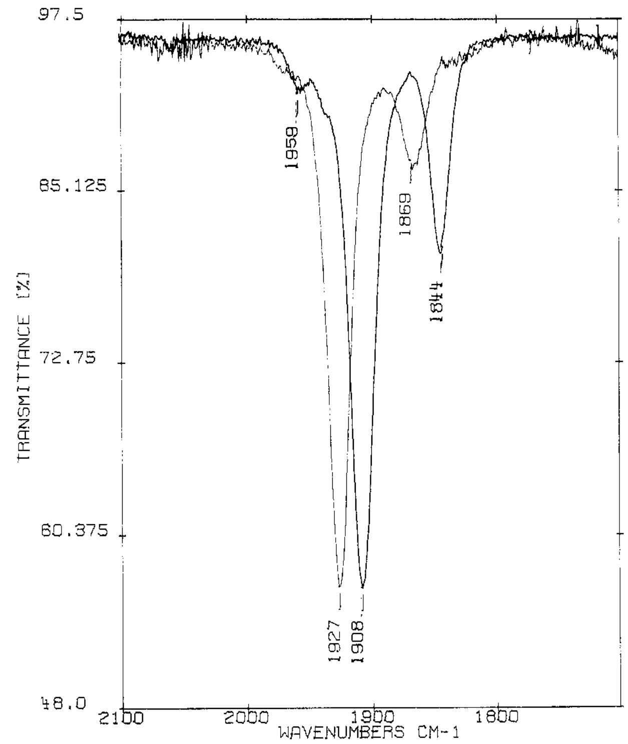
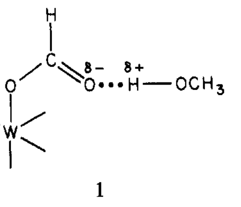


Figure 2. Infrared spectra in the ν(CO) region of $[HCO_2W(CO)_5^-][PPN]$ in methanol and in tetrahydrofuran. Lower frequency peaks are observed in THF solvent.

catalytic run.[17] Control experiments showed $M(CO)_6$ to be catalytically inactive under the reaction conditions, e.g., run 3 in Table I. The catalysts are actually more active than is indicated in Table I, since after only a few hours of catalysis the principal metal-containing species in solution is $M(CO)_6$. Thermal reactions of $HCO_2M(CO)_5^-$ in methanol in the absence of hydrogen do not yield HCO_2Me, hence indicating a previously suggested pathway for processes of this type (eq 5) to be of little consequence in this instance.[18,19]

$$HCO_2M(CO)_5^- + MeOH \nrightarrow HOM(CO)_5^- + HCO_2Me \quad (5)$$

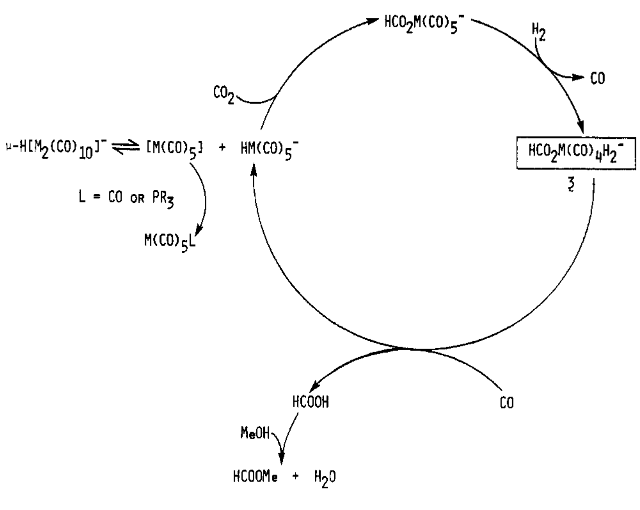
Although reaction 5 does not occur, interaction between $HCO_2M(CO)_5^-$ and methanol was observed via infrared spectroscopy. Figure 2 illustrates the infrared spectra in the ν(CO) region of $[PPN][HCO_2W(CO)_5]$ in tetrahydrofuran and in methanol, where a significant shift of all three ν(CO) bands to higher frequencies takes place in the latter solvent. This is interpreted in terms of hydrogen bonding between the unbound oxygen atom of the formate moiety and methanol as depicted in **1**. Disruption of this weak interaction was observed upon vacuum removal of methanol. An analogous infrared spectral shift was noted for the acetato derivative.



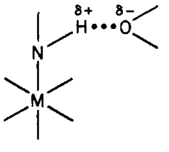
1

Interactions of the type described in **1** serve to neutralize the negative charge on the distal oxygen atom of the formate ligand in much the same manner as alkali metal ions. In a related system we have observed that the carboxylate ligand in $CH_3CO_2W(CO)_5^-$ is alkylated or lithiated by MeI or LiCl to provide $XW(CO)_5^-$ and CH_3CO_2Me or $LiCH_3CO_2$, respectively.[20] Reactions of this category are rather general and have been elaborated upon elsewhere.[21]

Scheme I



Similar but opposite spectral occurrances in neutral amine metal carbonyl derivatives (**2**) where the electron flow is in the opposite direction have been reported.[22-24]



2

Although methanol is not capable of protonating the metalloformate species to afford formic acid and $(CO)_5MOCH_3^-$, stronger acids such as CCl_3COOH effect this process (eq 6).

$$HCO_2W(CO)_5^- + CCl_3COOH \rightarrow HCOOH + CCl_3CO_2W(CO)_5^- \quad (6)$$

Scheme I summarizes a reaction pathway which accommodates these observations in a manner consistent with demonstrated chemical phenomena. As would be anticipated, HCOOH, the initially observed product, subsequently rapidly reacts with alcohols under the conditions of catalysis to afford alkyl formates and water. The reverse of this process is employed in the catalytic production of HCOOH from methanol and CO.[11] When the reaction was carried out in benzene solvent, formic acid was identified by gas chromatography; however, the yield of formic acid was less than would be anticipated on the basis of the yield of methyl formate when methanol was used as solvent.

Oxidative addition of hydrogen with concomitant reductive elimination of the hydrido formato ligands or ligand-assisted heterolytic splitting of dihydrogen with loss of formic acid constitute the main energy barrier in the catalytic cycle, since all other steps have been demonstrated to readily occur.[25-27] Species **3**

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(17) These measurements were carried out in a Flow-Thru cylindrical internal reflectance zinc selenide rod cell generously supplied by Barnes Analytical (Stamford, CT, 06906).

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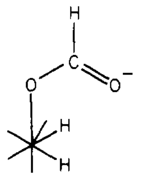
is defined explicitly as **4** and **5** for these two possibilities, respectively. Congruous with this supposition, reactions performed in the presence of added carbon monoxide (runs 6 and 7 in Table I) display greatly diminished activity toward formate production. Because dissociative loss of carbon monoxide in the $RCO_2M(CO)_5^-$ species is so facile, as evidenced by ^{13}CO exchange studies,CO loss is thought to occur prior to the addition of H_2 to the metal center. A pathway involving the intermediacy of hydrido carboxylates has been proposed previously for a variety of processes.[28,29] Indeed $W(CO)_5O_2CCH_3^-$ was found in this study to be a catalyst in the CO_2/H_2 reaction in methanol, with elimination of CH_3CO_2H occurring in the opening cycle (identified as the product of reaction with methanol, $CH_3CO_2CH_3$). Subsequent cycles afforded HCO_2Me with the same activity as observed employing $HCO_2W(CO)_5^-$ as catalyst (see runs 2 and 5).



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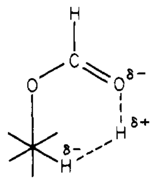

5

Consistent with Scheme I, $CH_3CO_2W(CO)_5^-$ *in the absence of carbon dioxide* under a loading pressure of 500 psi of dihydrogen afforded 0.8 mol of CH_3CO_2Me per mol of catalyst in methanol solvent. Similar hydrogenation processes attempted utilizing $HCO_2W(CO)_5^-$ in the absence of CO_2 did not result in production of HCO_2Me, because under these conditions decarboxylation (the reverse of reaction 1) is a more facile reaction than addition of hydrogen accompanied by elimination of formic acid. This was in fact demonstrated in a reaction carried out with use of $H^{13}CO_2W(CO)_5^-$ as catalyst which showed complete loss of the label in the formate ligand, as revealed by FTIR measurements in the 1700–1500-cm^{-1} region, after short reaction times (10 min).

As indicated in Scheme I, addition of 1 equiv of triphenylphosphine to a solution containing μ-$H[W_2(CO)_{10}]^-$ as catalyst resulted in production of $W(CO)_5PPh_3$ with little decrease in catalytic activity (turnover no. = 12.3). On the other hand, excess quantities of triphenylphosphine greatly retarded the hydrocondensation reaction of carbon dioxide (e.g., tenfold excess of PPh_3 decreased the turnover no. to 2.4), with formation of bis phosphine derivatives of tungsten being observed.[30]

When reaction 3 was carried out with use of ethanol as solvent the results obtained were totally consistent with those observed in methanol; however, the catalytic activity for ethyl formate production was significantly diminished over that for methyl formate production (Table II). This reduction in catalytic activity is likely due to the better coordinating ability of ethanol which would be expected to inhibit addition of dihydrogen to the unsaturated metal species. A similar effect was noted when excess quantities of a good coordinating ligand, such as PPh_3, were added to a catalytic system (vide supra).

The observed difference (by a factor of 4) in the rates of alkyl formate production in ethanol vs. methanol allows for a further test of Scheme I. If HCOOH is produced prior to esterification in alcohols, and no formic acid is observed during catalysis, the rates of esterification must be fast relative to HCOOH formation. A control reaction demonstrated this to be the case. More importantly, the ratio of EtOOCH:MeOOCH for esterification of HCOOH in a 1:1 mixture of ethanol to methanol was approximately unity and the same as the ratio of esters found in a catalytic reaction carried out in this mixture of alcohols.[31]

Table II. Synthesis of Ethyl Formate by Catalytic Hydrogenation of Carbon Dioxide in Ethanol[a]

expt	catalyst	turnover no.
10	μ-$H[W_2(CO)_{10}]^-$	4.3
11	$HCO_2W(CO)_5^-$	4.4
12	$CH_3CO_2W(CO)_5^-$	0.5 (CH_3CO_2Et) 4.6 (HCO_2Et)
13	$CH_3CO_2W(CO)_5^{-b}$	0.9 (CH_3CO_2Et)

[a] Reaction conditions are the same as those described in Table I. [b] Reaction carried out in 500 psi of hydrogen with no added carbon dioxide.

A catalytic run performed in the absence of both hydrogen and carbon dioxide employing μ-$H[W_2(CO)_{10}]^-$ as catalyst and a 250-psi loading pressure of carbon monoxide resulted in an enhanced rate of methyl formate production (turnover rate of 76 being observed). Tungsten hexacarbonyl was the only metal-containing species observed by infrared spectroscopy at the end of a 24-h reaction period. Control experiments employing $W(CO)_6$ as catalyst precursor carried out under conditions otherwise identical with those above led to *no* alkyl formate synthesis. Although a detailed understanding of this specific example of the synthesis of formates by the reaction of alcohols and carbon monoxide must await further studies, the literature has several examples of these processes involving other metal catalysts.[32] In some of these studies the intermediacy of alkoxymetal carbonyls is proposed.[33] In this regard we are investigating the role of $CH_3OM(CO)_5^-$ and $CH_3OC(O)M(CO)_5^-$ derivatives in the catalytic processes reported herein.

An important consideration which cannot be overlooked here is the connection between reactions involving CO_2 and H_2 and the water–gas shift reaction. Since the water–gas shift reaction is a reversible process and is catalyzed by these same metal catalysts, there is concern that reactions of CO_2/H_2 are proceeding via CO produced by the reverse of the water–gas shift reaction. This is particularly true because of the much greater catalytic activity for methyl formate formation from CO/MeOH. However, we feel that our findings are not consistent with such a proposal. For example, only trace quantities of CO (less than 0.05% of total gas composition) are detected during the CO_2/H_2 reaction, which is substantially smaller than the equilibrium distribution of CO from the water–gas shift reaction. Furthermore, the hydrocondensation reaction of CO_2 is suppressed in the presence of large excesses of carbon monoxide. As an additional and more definitive check for the possible involvement of carbon monoxide in the methyl formate synthesis from the CO_2/H_2-catalyzed reaction, the completely ^{13}CO-labeled derivative, $HCO_2W(^{13}CO)_5^-$, was utilized as a catalyst. After a brief reaction period (10 min), the methyl formate detected by GC–MS was all $H^{12}CO_2Me$. A similar observation was noted for our ruthenium cluster catalyzed hydrogenation of carbon dioxide process, where $HCO_2Ru_3(^{13}CO)_{10}^-$ was employed as catalyst precursor.[34]

Experimental Section

All manipulations were carried out either in an argon dry box or on a double manifold Schlenk vacuum line under an atmosphere of dry nitrogen. Tetrahydrofuran, hexane, and dimethoxyethane (DME) were dried by refluxing over sodium benzophenone ketyl under nitrogen. Methanol and ethanol were dried by refluxing over magnesium followed by distillation. Routine infrared spectra were recorded in 0.10–1.0-mm

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matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with a Data Station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. For recording high-quality infrared spectra an IBM FTIR Model 85 spectrophotometer was used. GC-MS experiments were performed by using a Hewlett-Packard 5710A gas chromatograph coupled to an HP Model 5980 mass spectrometer operating with a Model 5933A data system.

Preparations. [PPN][μ-$H(M_2(CO)_{10})$], where M = Cr and W, were prepared by the procedure reported by Grillone and co-workers.[35] [PPN][$M(CO)_5Cl$] (M = Cr and W) and [PPN][$Cr(CO)_5O_2CH$] were synthesized as described previously.[4d,3] [PPN][$W(CO)_5O_2CH$] and [PPN][$W(CO)_5O_2CCH_3$] were prepared by reaction of [PPN][O_2CH][4f] or [PPN][O_2CCH_3][4f,36] with $W(CO)_6$ in refluxing DME for 30 min. After removal of DME solvent, THF was added to the yellow solids and the resulting solutions were filtered over celite. Crystals of pure compounds were obtained after addition of hexane to these THF solutions followed by overnight cooling. The complexes were isolated by filtration and dried under vacuum to provide yields of 65–75%. Carbon-13-labeled derivatives $H^{13}CO_2W(CO)_5^-$ and $HCO_2W(^{13}CO)_5^-$ were obtained by our previously published procedure.[3]

Reaction of [PPN][$W(CO)_5O_2CH$] with Cl_3CCOOH. [PPN][$W(CO)_5O_2CH$] (0.028 g, 31 μmol) was dissolved in 5 mL of THF under nitrogen followed by addition of 0.0315 g (193 μmol) of Cl_3COOH. The reaction mixture was stirred at ambient temperature and monitored by infrared spectroscopy in the ν(CO) region. After several minutes of reaction the peaks due to the $W(CO)_5O_2CH^-$ anion were shifted to higher frequencies, 1908 and 1844 cm^{-1} shifted to 1913 and 1852 cm^{-1}. The reaction was quantitative as indicated by the intensity of the ν(CO) infrared bands of the products.

Catalytic Reactions. In a typical run, 0.14 mmol of catalyst were dissolved in 15 mL of degassed methanol. After addition of the internal standard (hexane), the solution was placed inside a dry box and transferred to a 300-mL Parr reactor. This vessel was then removed from the dry box and pressurized up to 250 psi (at 25 °C) with pure CO_2. Molecular hydrogen was used to carry the pressure up to 500 psi. The reactor was heated by means of the mantle equipped with a Parr temperature controller Model 4831. When the temperature inside the reactor (measured with a thermocouple type J (Iron–constantan)) reached 125 °C, the clock was started. At the end of the reaction period (normally 24 h) the heating was discontinued and the reactor placed in an ice bath for 1 h. At this moment a gas sample was taken by allowing the gas to escape and collecting it using a glass sampling device. After putting the reactor inside a dry box, the vessel was opened and the reaction solution transferred to the IR cell and to a septum-capped vial in order to be analyzed by GC (Perkin-Elmer Model Sigma 2 equipped with a thermo-conductivity detector and a Cole-Palmer recorder Model 8385-32, the column used for analyses of liquid samples was 10% carbowax 20 m over chromosorb (2 m × $^1/_8$ in.), 50 °C (1 min) to 130 °C at 25 °C/min, inlet pressure 21 psi of He; for gas samples the column used was carbosphere, 100 °C (1.5 min) to 160 °C (2 min) at 25 °C/min).

The high-pressure infrared measurements were carried out with use of the same Parr reactor as well as the same loading procedures. The high-pressure IR cell (CIR cell) used was provided by Barnes Analytical. The reactor was connected to the cylindrical internal reflection cell by means of $^1/_{16}$-in. tubing, and the sample was delivered directly from the reactor to the cell with both being maintained at the pressure of the reactor. Background spectra were determined in a completely analogous manner in the absence of catalyst.

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Registry No. μ-$H[W_2(CO)_{10}]^-PPN^+$, 56172-01-1; $HCO_2W(CO)_5^-PPN^+$, 36499-81-7; $W(CO)_6$, 14040-11-0; $ClW(CO)_5^-PPN^+$, 39048-34-5; $CH_3CO_2W(CO)_5^-PPN^+$, 36515-92-1; μ-$H[Cr_2(CO)_{10}]^-PPn^+$, 62314-83-7; $HCO_2Cr(CO)_5^-PPn^+$, 82880-57-7; HC(O)OMe, 107-31-3; CO_2, 124-38-9; HC(O)OEt, 109-94-4; H_2, 1333-74-0; $H^{13}CO_2W(CO)_5^-$, 90065-85-3; $HCO_2W(^{13}CO)_5^-$, 90065-86-4.

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Synthesis of a Chelated Tungsten–Carbene–Alkene Complex and Its Conversion to a Cyclopropane

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Abstract: Reaction of $(CO)_5W{=}C(OCH_3)C_6H_4$-*p*-CH_3 with 1-amino-2,2-dimethyl-3-butene (**8**) gave a 3:1 mixture of the *Z* and *E* isomers of pentacarbonyl [((2,2-dimethyl-3-butenyl)amino)(*p*-tolyl)carbene]tungsten(0) (**10**-*Z* and **10**-*E*). Thermolysis of **10** did not produce a metal–carbene–alkene complex but rather led to formation of an imine decomposition product. N-Methylation of **10** by treatment with lithium diisopropylamide and methyl iodide produced a mixture of the *Z* and *E* isomers of pentacarbonyl [((*N*,2,2-trimethyl-3-butenyl)amino)(*p*-tolyl)carbene]tungsten(0) (**13**-*Z* and **13**-*E*). Thermolysis of **13** in benzene at 88 °C led to formation of the tungsten–carbene–alkene complex tetracarbonyl[(((*Z*)-η^2-*N*,2,2-trimethyl-3-butenyl)amino)(*p*-tolyl)carbene]tungsten(0) (**6**). Further heating of **6** gave the cyclopropane 1-*p*-tolyl-2,4,4-trimethyl-2-azabicyclo[3.1.0]hexane (**7**). The X-ray crystal structure of **6** shows two independent molecules per unit cell; in one molecule, the carbene and alkene ligands are approximately parallel and in the other they are approximately perpendicular. Crystal data for **6**: space group $P2_1$, $Z = 4$, $a = 10.287$ (3) Å, $b = 11.651$ (3) Å, $c = 16.319$ (5) Å, $\beta = 98.83$ (2)°, $R = 0.039$, and $R_w = 0.053$ for the 4295 reflections with $F_o > 3\sigma(F_o)$. ^1H NMR of **6** revealed fluctional processes attributed to slow rotation of the *p*-tolyl group and to reversible decomplexation of the alkene ligand of **6**. PPh_3 reversibly displaces the alkene ligand of **6** and also accelerates cyclopropane formation from **6**.

Metal–carbene–alkene complexes have been proposed as important intermediates in the olefin metathesis reaction,[1] in the cyclopropanation[2] of alkenes, and in Ziegler–Natta polymerization of alkenes.[3] Examples of chelated[4-9] and nonchelated[10,11] metal–carbene–alkene complexes are known, but most of these com-

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