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A Titanacyclobutane Precursor to Alkyl-Substituted Titanium–Carbene Complexes[†]

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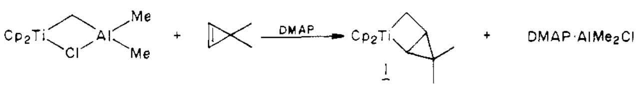
The preparation of metallacycle 1 by the addition of 3,3-dimethylcyclopropene to precursors of "$Cp_2Ti{=}CH_2$" (Cp = η^5-C_5H_5) is described. Reaction of 1 with benzophenone affords 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene as the only organic product. When phosphines $PMeR_2$ (R = Me, Ph) are added to 1, the phosphine adducts $(PMeR_2)Cp_2Ti{=}CHCMe_2CHCH_2$ (**2**) are obtained. Reaction with dimethylaluminum chloride affords a heterobimetallic alkylidene complex, $Cp_2\overline{TiCH(CMe_2CHCH_2)AlMe_2Cl}$ (**3**). The observed reactivity of 1 is consistent with productive cleavage of the metal-containing ring to "$Cp_2Ti{=}CHC(Me_2)_2CHCH_2$".

Although synthetic routes to α-alkyl-substituted zirconium–carbene compounds[1] and to bimetallic bridged alkylidene complexes[2,3] have been described, none of the reported methods have proven useful for the isolation of the analogous titanium compounds.[4] Schwartz and Hartner[2] have observed ^{1}H NMR signals attributable to a propylidene-bridged bimetallic complex on addition of an organoaluminum hydride compound to a titanocene–alkenyl complex; however, paramagnetic impurities prevented full characterization. Yoshida[3] has observed reactivity consistent with the aluminum adduct of a titanocene–carbene complex on addition of alkenylaluminum compounds to titanocene dichloride. Synthesis of substituted analogues of the Tebbe reagent[5] by the same method used to prepare it failed, presumably due to the presence of β-hydrogens.[6] The only monometallic carbene complexes of titanium reported to date are phosphine adducts of the parent methylidene compound.[1,7] We describe herein the synthesis of a crystalline α-substituted titanocene–carbene complex from its parent metallacycle.

Since thermolysis of titanacyclobutanes generally affords products consistent with metathesis-type cleavage rather than the products of β-hydrogen chemistry or reductive elimination,[8] they seemed to be reasonable precursors of α-substituted titanocene–carbene compounds. However, cleavage of bis(cyclopentadienyl)-α,β-dimethyltitanacyclobutane resulted primarily in loss of 2-butene.[9] The productive reaction, loss of propene to give titanocene ethylidene, was only a minor pathway. Similarly, thermolysis of the α,β-disubstituted metallacycle derived from the addition of cyclopentene to "$CpTi{=}CH_2$" yielded cyclopentene quantitatively.[10] Presumably, the predominance of the nonproductive cleavage is due to adverse steric interactions in α-substituted carbene compounds relative to the unsubstituted parent compound. We hoped to enhance the productive cleavage pathway by preparing the precursor titanacyclobutane from a highly strained, cyclic olefin.

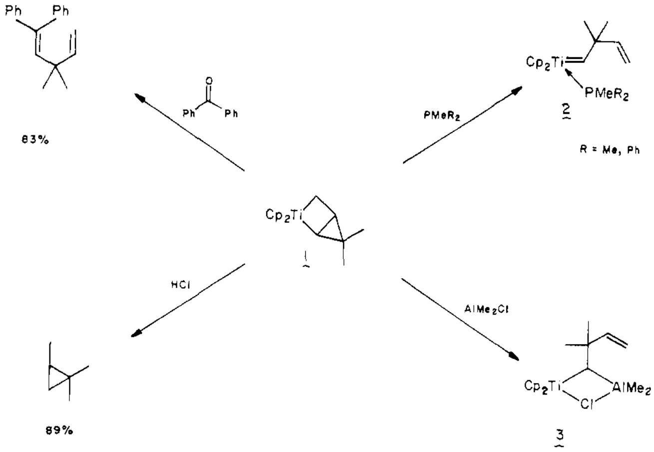
Results and Discussion

Reaction of the Tebbe reagent[5] with 3,3-dimethylcyclopropene and (dimethylamino)pyridine (DMAP) affords titanacycle 1 as red needles in 33% isolated yield.[11]



Compound 1 was stable at 23 °C as a solid but slowly decomposed in solution with a half-life of approximately 1 week. Proton NMR analysis of 1 showed the α-proton[12] at δ 4.90 and the β-proton at δ −0.28. The diastereotopic α'-protons occur at δ 2.39 and 2.03 with the expected coupling patterns. A high-field β-proton and low-field α-protons are characteristic of the titanacyclobutane

Scheme I



[†] Contribution No. 7244.

(1) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640.

(2) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.

(3) Yoshida, T. *Chem. Lett.* **1982**, 429.

(4) Related compounds have been obtained. See: Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *Ibid.* **1984**, *106*, 5178. Buchwald, S. L.; Grubbs, R. H. *Ibid.* **1983**, *105*, 5490.

(5) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(6) Tebbe, F. N.; Guggenberger, J. *J. Chem. Soc., Chem. Commun.* **1973**, 227, as discussed in ref 2.

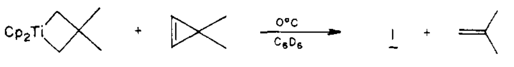
(7) The PMe_3, PMe_2Ph, and PEt_3 adducts of titanocene methylene have been isolated and an X-ray structural analysis is in progress. Meinhart, D.; Grubbs, R. H., unpublished results.

(8) (a) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876.

(9) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9.

(10) Grubbs, R. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, pp 532, 547.

(11) Metallacycle 1 can also be prepared by olefin exchange from other titanacyclobutanes. For example



(12) Ring positions of metallacycle 1 are discussed as shown.

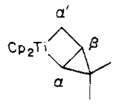


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Table I. Selected NMR Spectroscopic Data[a]

complex	H[b]	C[b]	J_{HP}[c]	J_{CP}[c]	J_{CH}[c]
1	4.90	134.82			149
2a	12.06	306.90	7.3	26.6	111
2b	13.23	309.38	6.8	24.9	115
2c	12.32	312.20	5.9	23.5	110
3	9.78	225.83			116

[a] NMR solvent was C_6D_6. [b] In ppm relative to solvent. [c] In Hz.

structure.[8,9] Signals assigned as the two inequivalent Cp groups and the two inequivalent methyl groups appear in the appropriate regions of the spectrum. The chemical shift of the α-carbon (δ 134.82) occurs at low field while that of the β-carbon occurs at δ 18.43. The large C–H coupling observed for the β-carbon, J = 170 Hz, is similar to those generally obtained in cyclopropane ring systems.[13] Interestingly, the J_{CH} for the α-position (149 Hz) is close to that at the α'-position (145 Hz) even though the α-carbon is in a three-membered ring. Additional evidence for the formulation of 1 as shown was provided by the acidolysis of 1. Reaction with HCl at −50 °C yielded 1,1,2-trimethylcyclopropane as the only organic product. No 3,3-dimethyl-1-butene was observed.

When metallacycle 1 was stirred at 23 °C with benzophenone, 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene was obtained in high yield (Scheme I). Many of the previously reported titanacyclobutanes have proven to be useful synthetic reagents for the methylenation of ketones.[14] Thermolysis of the metallacycles generally affords olefin and "$Cp_2Ti{=}CH_2$" which then reacts in a manner analogous to other early-transition-metal carbenes[15]—exchanging the methylidene fragment with the carbonyl oxygen of added ketones. In the case of metallacycle 1, isolation of 3,3-dimethyl-1,1-diphenyl–1,4-pentadiene suggests intermediacy of the α-substituted carbene "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$". Since no 1,1-diphenylethylene was obtained, the productive cleavage must be greatly favored over the nonproductive reaction to give "$Cp_2Ti{=}CH_2$".

Upon reaction of 1 at room temperature with appropriate alkylphosphine compounds, the monophosphine adducts of the α-substituted titanium–carbene complex were obtained. Complexes containing trimethylphosphine (**2a**) and dimethylphenylphosphine (**2b**) were cleanly isolated as tan powders. The ^1H and ^{13}C NMR data of **2a** and **2b** are consistent with the proposed structures. Signals for H_α and C_α are found at low field (see Table I) as reported for other high-valent (nucleophilic) carbenes.[16] For example, the signals for the carbene carbons of $Cp_2ClTa{=}CHCMe_3$,[16d] $(t\text{-}BuCH_2O)_2Br_2W{=}CHCMe_3$,[16a] and $Cp_2(PPh_3)Zr{=}CHCMe_3$[1] are found at 273, 299, and 270 ppm, respectively. The observed values of J_{CH} at the α-position of 2 are much smaller than expected for an sp^2-hybridized carbon. Presumably, this is due to a deformation of the β tertiary center to reduce the adverse interaction with the cyclopentadienyl ligand required by the preferred geometry[17] of early transition-metal carbene species.[18] The resulting increased Ti–C–C bond angle yields greater p character in the C_α–H_α bond. The electronic demands of the titanium–carbon double bond may also lower the J_{CH} at the α-position.[19] Both **2a** and **2b** decompose slowly in solution at room temperature. The half-life for **2a** is 3–4 days while that for **2b** is roughly 1 day.

In contrast to reaction with PMe_3 and $PPhMe_2$, reaction of 1 with $PMePh_2$ does not go to completion. The $PMePh_2$ complex **2c** is formed in equilibrium with metallacycle 1.[21] The equilibrium constant was measured as 10.5 ± 0.5 L·mol^{-1} corresponding to a $\Delta G°_{296}$ = 1.4 (1) kcal/mol^{-1}. NMR spectroscopic data for **2c** are similar to that discussed above for the other phosphine adducts. No adduct formation is observed when 1 is stirred with PPh_3 even after heating to 45 °C. This trend is attributable to the increased steric demands of the larger phosphines and to their lowered basicity.

A bimetallic alkylidene-bridged complex analogous to the Tebbe reagent was obtained when $AlMe_2Cl$ was added to titanacycle 1. In contrast to the reactivity of 1 with phosphines or with benzophenone, this reaction was rapid at −40 °C. One explanation is a strong assistance by $AlMe_2Cl$ in the ring-opening reaction.[22] Low-temperature NMR data for 3 are included in Table I and in the Experimental Section. The two cyclopentadienyl groups, the aliphatic methyl groups, and the two aluminum-bonded methyl groups are inequivalent. The chemical shifts of H_α and C_α are similar to reported data for related compounds.[2,3,5] In the case of 3, the J_{CH} of 116 Hz is a reasonable value for an sp^3-hybridized carbon attached to the electrophilic Ti and Al centers. The purple, crystalline complex 3 is less stable than the phosphine adducts, decomposing in solution at temperatures above 10 °C. Metallacycle 1 was not regenerated.

The strain energy of the cyclopropene ring system has been estimated at 52–55 kcal/mol.[23] In view of this large value, cyclopropenes are expected to be reactive toward transition metals. Reactions with low-valent transition metals generally result in either 2,3 carbon–carbon single bond cleaving reactions or in cyclooligomerizations at the

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[13] J_{CH} for cyclopropane is 161 Hz. Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.

[14] (a) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

[15] For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Kauffmann, T.; Ennen, B.; Sander, J.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 244. (c) Reference 1. (d) Reference 5.

[16] For examples, see: (a) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. (b) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440. (c) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73. (d) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (e) Reference 15a. (f) Reference 1.

[17] Calculations suggest that titanium carbenes $X_2Ti{=}CH_2$ prefer a planar structure.[26]

[18] This argument was proposed by Schrock[15a] to explain low J_{CH} values in 18-electron Ta and Nb carbene complexes. Such a deformation would increase the Ti=C—C bond angle and, consequently, would increase the p character in the C_α–H_1 bond.

[19] Observed J_{CH} in unsubstituted group IV phosphine–carbene adducts include (a) $Cp_2Ti{=}CH_2$, the PMe_3 adduct has J_{CH} = 124 Hz.[7] (b) $Cp_2Zr{=}CH_2$, the $PMePh_2$ adduct has J_{CH} = 121 Hz.[20]

[20] Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1.

[21] Observation of this equilibrium suggests the reversibility of metallacycle cleavage in 1.

[22] Such assistance by $AlMe_2Cl$ was proposed for its reaction with $Cp_2\overline{TiCH_2CH(t\text{-}Bu)CH_2}$. Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942.

[23] Wiberg, K. B. *Isr. J. Chem.* **1983**, *23*, 85. Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976; p 273. Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

double bond which preserve the three-membered ring.[24] The only reported example of reaction resulting in cleavage of the double bond involved addition of 3,3-dimethylcyclopropene to a rhodium dimer.[25] In the case of "$Cp_2Ti{=}CH_2$", initial [2 + 2] addition to the double bond followed by ring cleavage results in overall fragmentation of the double bond of dimethylcyclopropene.

Since the strain energy of cyclopropane (27–28 kcal/mol)[23] can be used as a lower limit of the inherent strain in the ring system of titanacycle 1, it is perhaps surprising that 1 is stable enough with respect to ring cleavage to permit isolation. The observed stability of previously reported titanacyclobutanes relative to titanium carbene compounds has been discussed in terms of electronic factors.[26] Nonproductive cleavage of 1 to "$Cp_2Ti{=}CH_2$" requires loss of the highly strained olefin. The experimental evidence discussed above clearly excludes that pathway. Cleavage of 1 to "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$" is favored by relief of ring strain; however, this productive cleavage places a tertiary center in the β-position of the titanium carbene. Since the preferred geometry of titanium carbene compounds requires an adverse interaction of the α-substituent and a cyclopentadienyl group, the overall energy of the cleavage product is increased. Once the carbene is formed, the absence of β-hydrogens and steric barrier to dimerization may enhance its kinetic stability. Hence, a balance of structural and electronic effects permit isolation of both titanacyclobutane 1 and adducts of the isomeric α-substituted carbene compound.

Further work in this area will include an extension of these investigations to other cyclic olefins and an examination of the suitability of 1 as a metathesis catalyst.

Experimental Section

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

Tebbe reagent[5,8a] and 3,3-dimethylcyclopropene[27] were prepared according to published procedures. (Dimethylamino)pyridine (Aldrich) and benzophenone (Aldrich) were recrystallized from hot toluene. The 3,3-dimethyl-1-butene was purchased from Aldrich Chemical Co. The 1,1,2-trimethylcyclopropane was purchased from Chemical Samples Co. Trimethylphosphine (Strem), dimethylphenylphosphine (Aldrich), and methyldiphenylphosphine (Strem) were used without further purification. Dimethylaluminum chloride (Texas Alkyls Co.) was used as a 2.5 M solution in toluene. Dichloromethane was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over H_2SO_4, dried over CaH_2, and vacuum-transferred onto sodium–benzophenone ketyl. Benzene was dried over CaH_2, degassed, and vacuum-transferred onto sodium–benzophenone ketyl. Diethyl ether, toluene, and benzene-d_6 (Cambridge Isotope Laboratories) were degassed and stirred over sodium–benzophenone ketyl. The dried and degassed solvents were vacuum-transferred into dry vessels equipped with Teflon valve closures and stored under Ar. Reagent grade petroleum ether (35–60 °C) was used without further purification.

NMR spectra were recorded on a JEOL FX-90Q (89.60-MHz ^1H; 22.53-MHz ^{13}C; 36.27-MHz ^{31}P) NMR spectrometer or on a JEOL GX-400 (399.65-MHz ^1H; 100.40-MHz ^{13}C) NMR spectrometer. Chemical shifts for ^1H and ^{13}C spectra are reported vs. residual solvent signals. Chemical shifts for ^{31}P are reported relative to external 85% H_3PO_4. Temperatures were measured by using $\Delta\nu$ (CH_3OH) and were accurate to +0.2 °C. Difference NOE spectra were obtained by using standard procedures.[28] Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary used and equipped with a Hewlett-Packard Model 3390A integrator and a 0.33 mm × 40 m SE30 capillary column. Infrared analyses utilized a Shimadzu IR-435 infrared spectrophotometer.

Preparation of Metallacycle 1. Approximately 1.5 g (22.0 mmol) of 3,3-dimethylcyclopropene was vacuum-distilled onto 1.5 g (12.6 mmol) of (dimethylamino)pyridine (DMAP). The mixture was dissolved in CH_2Cl_2 (10 mL) and stirred at −20 °C. A −20 °C solution of Tebbe reagent (3.0 g, 10.5 mmol) in 5.0 mL of CH_2Cl_2 was added. After 30 min, the red solution was added dropwise to 150 mL of vigorously stirred pentane at −30 °C. The precipitated DMAP–$AlMe_2Cl$ adduct was removed by rapid filtration, and the filtrate was evaporated to dryness under vacuum. The resultant solid was crystallized from diethyl ether by slow cooling to give 0.89 g (33%) of 1 as red needles. ^1H NMR (90 MHz, C_6D_6): δ 5.46 (s, 5 H, Cp), 5.26 (s, 5 H, Cp), 4.90 (d, 1 H, J_{HH} = 10.3 Hz, H_α), 2.39 (dd, 1 H, J_{HH} = 10.7, 8.4 Hz, $H_{\alpha'}$), 2.03 (pt, 1 H, J_{HH} = 8.4, 8.4 Hz, $H_{\alpha'}$), 1.42 (s, 3 H, Me), 1.03 (s, 3 H, Me), −0.28 (ddd, 1 H, J_{HH} = 10.3, 10.7, 8.4 Hz, H_β). Difference NOE (400 MHz, C_6D_6): irradiation of the signal at δ 5.46 (Cp) enhances signals at δ 2.03 ($H_{\alpha'}$-cis) and 1.03 (Me); irradiation of the signal at δ 5.26 enhances signals at δ 4.90 (H_α), 2.39 ($H_{\alpha'}$-trans), and −0.28 (H_β). ^{13}C NMR (90 MHz, C_6D_6): δ 134.82 (d, J_{CH} = 149 Hz, C_α), 107.46 (d, Cp), 107.07 (d, Cp), 62.56 (t, J_{CH} = 145 Hz, $C_{\alpha'}$, 61.13 (quaternary), 35.53 (q, Me), 20.19 (q, Me), 18.43 (d, J_{CH} = 170 Hz, C_β). IR (C_6D_6): 3090 (w), 3010 (w), 2940 (s), 2850 (w), 1440 (m), 1363 (m), 1290 (w), 1017 (s), 823 (sh), 796 (s), 752 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{20}Ti$: C, 73.85; H, 7.75. Found: C, 73.53; H, 7.59.

Reaction of 1 with Benzophenone. To a solution of 1 (50 mg, 0.19 mmol) in 1.0 mL of toluene at 0 °C was added benzophenone (39 mg, 0.21 mmol). The reaction mixture was warmed to 23 °C, stirred at 23 °C for 10 h, and then diluted with 10 mL of petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under reduced pressure afforded a colorless oil. Identification of the product as 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene was based on comparison of the ^1H NMR data with published data[29] and on a high-resolution mass spectrum; yield 40 mg (83%).

Acidolysis of 1. HCl was generated by the addition of NaCl (25 mg, 0.43 mmol) to 1.5 mL of concentrated H_2SO_4. The evolved gas was vacuum-transferred onto titanacycle 1 (50 mg, 0.19 mmol) in 2.0 mL of toluene. The reaction flask was isolated by means of a Teflon needle valve and warmed to −50 °C. After 15 min, the volatiles were removed by vacuum distillation. Cyclohexane (10 μL, 0.09 mmol) was added to the volatiles, and the products were quantitated by capillary VPC. The single volatile product 1,1,2-trimethylcyclopropane was identified by coelution with an authentic sample: yield 0.17 mmol (89%).

Preparation of PMe_3 Adduct 2a. To 1 (100 mg, 0.38 mmol) in 2.0 mL of benzene was added 60 μL of PMe_3 (0.76 mmol). The solution was stirred at 23 °C for 1.5 h. Removal of the volatiles in vacuo afforded a brown oil. The flask was cooled to −78 °C, and its contents were triturated with 0.5 mL of −78 °C pentane. The added pentane was removed in vacuo. Phosphine adduct **2a** was obtained as a tan powder (63 mg, 50%). ^1H NMR (400 MHz, C_6D_6): δ 12.06 (d, 1 H, J_{HP} = 7.3 Hz, H_α), 6.24 (dd, 1 H, J_{HH} = 17.5, 10.4 Hz, $CHCH_2$), 5.35 (d, 5 H, J_{HP} = 2.4 Hz, Cp),

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[24] Binger, P.; Cetinkaya, M.; Doyle, M. J.; Germer, A.; Schuchardt, U. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 271 and references therein. Newton, M. G.; Pantaleo, N. S.; King, R. B.; Chu, C.-K. *J. Chem. Soc., Chem. Commun.* **1979**, 10. Dettlaf, G.; Behrens, U.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3019. Fiato, R. A.; Mushak, P.; Battiste, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 869 and references therin.

[25] Schaverien, C. J.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, *16*, 912.

[26] Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206. Rappé, A. K.; Upton, T. H. *Organometallics* **1984**, *3*, 1440. Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297. For related references, see: Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 281, 815. Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582.

[27] Binger, P. *Synthesis* **1974**, 190.

[28] Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703. Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 353.

[29] Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775.

5.33 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.05 (dd, 1 H, J_{HH} = 17.5, 1.8 Hz, CHC*H*H), 4.96 (dd, 1 H, J_{HH} = 10.4, 1.8 Hz, CHCH*H*), 1.27 (s, 3 H, Me), 1.18 (s, 3 H, Me), 0.80 (d, 9 H, J_{HP} = 6.3 Hz, PMe_3). ^{13}C NMR (100.4 MHz, C_6D_6): δ 306.90 (J_{CP} = 26.6 Hz, J_{CH} = 111 Hz, C_α), 151.83 (J_{CP} = 4.5 Hz, *C*HCH_2), 106.55 (CH*C*H_2), 102.42 (Cp), 99.85 (Cp), 56.28 (quaternary), 31.41 (J_{CP} = 4.4 Hz, Me), 30.42 (J_{CP} = 6.0 Hz, Me), 20.44 (J_{CP} = 17.7 Hz, PMe_3). IR (C_6D_6): 3070 (w), 2940 (s), 2900 (s), 2850 (m), 1625 (w), 1420 (m), 1365 (w), 1298 (w), 1279 (m), 1020 (sh), 1010 (m), 942 (s), 933 (sh), 892 (m), 818 (w), 790 (vs), 780 (sh), 720 (w), 710 (s), 660 (w) cm^{-1}; ^{31}P NMR (36.27 MHz, C_6D_6: δ +11.91. Anal. Calcd for $C_{19}H_{29}TiP$: C, 67.86; H, 8.70. Found: C, 67.83; H, 8.18.

Preparation of PMe_2Ph Adduct 2b. The adduct **2b** was prepared by the same procedure described for **2a** using $PPhMe_2$ (60 μL, 0.42 mmol). Phosphine adduct **2b** was obtained as a tan powder (84 mg, 55%). ^1H NMR (400 MHz, C_6D_6): δ 13.23 (d, 1 H, J_{HP} = 6.8 Hz, H_α), 7.22–7.09 (m, 5 H, Ph), 6.22 (dd, 1 H, J_{HH} = 10.6, 17.6 Hz, C*H*CH_2), 5.46 (s, 5 H, Cp), 5.37 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.07 (d, 1 H, J_{HH} = 17.6, CHC*H*H), 4.96 (d, 1 H, J_{HH} = 10.6 Hz, CHCH*H*), 1.30 (s, 3 H, Me), 1.29 (d, 3 H, J_{HP} = 6.8 Hz, P*Me*MePh), 1.21 (s, 3 H, Me), 1.18 (d, 3 H, J_{HP} = 6.4 Hz, PMe*Me*Ph). ^{13}C NMR (100.4 MHz, C_6D_6): δ 309.38 (J_{CP} = 24.9 Hz, J_{CH} = 115 Hz, C_α), 151.80 (J_{CP} = 3.0 Hz, *C*HCH_2), 140.92 (J_{CP} = 13.2 Hz), 131.52 (J_{CP} = 10.3 Hz), 129.11, 128.34, 106.71 (CH*C*H_2), 102.96 (Cp), 100.17 (Cp), 56.67 (J_{CP} = 3.0 Hz, quaternary), 31.68 (J_{CP} = 4.4 Hz, Me), 30.40 (J_{CP} = 5.8 Hz, Me), 21.59 (J_{CP} = 22.1 Hz, P*Me*MePh), 20.01 (J_{CP} = 20.5 Hz, PMe*Me*Ph). ^{31}P NMR (36.27 MHz, C_6D_6): δ +25.10. IR (C_6D_6): 3015 (w), 2950 (s), 2900 (m), 2860 (w), 1625 (w), 1480 (w), 1465 (w), 1432 (s), 1365 (m), 1285 (w), 1275 (w) 1091 (w), 1065 (w), 1015 (s), 937 (m), 900 (s), 825 (w), 792 (vs), 740 (s), 722 (w), 692 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{31}TiP$: C, 72.35; H, 7.84. Found: C, 72.12; H, 7.59.

Reaction of 1 and PPh_2Me. To a 5-mm NMR tube containing **1** (10 mg, 0.04 mmol) in 0.5 mL of benzene-d_6 was added 20 μL of PPh_2Me (0.10 mmol). The tube was placed in the probe of the JEOL-GX400 NMR instrument, and the reaction was monitored by ^1H NMR spectroscopy. The reaction was observed to reach an equilibrium between **1** and its PPh_2Me adduct **2c**, with an approximate ratio of 1:1, within 1 h. ^1H NMR (400 MHz, C_6D_6) assignment based on exclusion of peaks attributable to **1**: δ 12.32 (d, 1 H, J_{HP} = 5.9 Hz, H_α), 7.22–7.02 (m, 10 H, Ph), 6.14 (dd, 1 H, J_{HH} = 17.6, 10.5 Hz, C*H*CH_2), 5.49 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.36 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.12 (d, 1 H, J_{HH} = 17.6 Hz, CHC*H*H), 4.97 (d, 1 H, J_{HH} = 10.5 Hz, CHCH*H*), 1.65 (d, 3 H, J_{PH} = 6.0 Hz, PMe), 1.38 (s, 3 H, Me), 1.26 (s, 3H, Me). ^{13}C NMR (100.4 MHz, C_6D_6): δ 312.20 (J_{CP} = 23.5 Hz, J_{CH} = 110 Hz, C_α).

Equilibrium Measurements. To each of three 5-mm NMR tubes was added 400 μL of a 0.096 M solution of **1** in benzene-d_6 (10 mg of **1** to each). One, two, and four equivalents (7.2, 14.3, and 28.6 μL) of $PMePh_2$ were added to the tubes along with additional benzene-d_6 to bring the volume of the contents of each tube to 450 μL. The samples were stored at −20 °C until use. Each tube was placed in the probe of the JEOL-GX400. The reactions were monitored by ^1H NMR spectroscopy until no change was observed for 30 min. All samples required less than 1.5 h to reach equilibrium. The equilibrium ratio was measured by integration of the doublet at δ 4.90 (H_α of **1**) and the doublet at δ 4.97 (CHCH*H* of **2c**). The three derived equilibrium constants were averaged to obtain the reported constant.

Preparation of the $AlMe_2Cl$ Adduct 3. To a −40 °C solution of **1** (250 mg, 0.96 mmol) in 2.0 mL of toluene was added 400 μL of a 2.5 M $AlMe_2Cl$ solution (1.0 mmol of $AlMe_2Cl$). An immediate color change from red to purple was observed. After 30 min at −40 °C, the volatiles were removed in vacuo at −10 °C yielding a drak purple solid. The solid was redissolved in −10 °C pentane. A small amount of insoluble material was discarded. Slow cooling of the pentane solution to −50 °C afforded 95 mg (28%) of **3** as a purple powder. Solid **3** was stored at −40 °C. In solution, **3** is unstable at temperatures above 10 °C. ^1H NMR (90 MHz, C_6D_6, 10 °C): δ 9.78 (s, 1 H, H_α), 6.63 (dd, 1 H, J_{HH} = 16.6, 10.0, C*H*CH_2), 5.85 (s, 5 H, Cp), 5.61 (s, 5 H, Cp), 5.04 (d, 1 H, J_{HH} = 16.6, CHC*H*H), 5.01 (d, 1 H, J_{HH} = 10.0, CHCH*H*), 1.20 (s, 3 H, Me), 0.96 (s, 3 H, Me), −0.13 (s, 3 H, Al*Me*Me), −0.24 (s, 3 H, AlMe*Me*). ^{13}C NMR (22.5 MHz, C_6D_6, 10 °C): δ 225.83 (d, J_CH = 116 Hz, H_α), 150.51 (d, *C*HCH_2), 113.33 (d, Cp), 111.12 (d, Cp), 109.12 (t, *C*HCH_2), 59.13 (quaternary), 34.83 (q, Me), 30.99 (q, Me), −4.7 (br q, H_{CH} = 115 Hz, $AlMe_2$). Anal. Calcd for $C_{18}H_{26}TiAlCl$: C, 61.29; H, 7.43. Found: C, 60.96; H, 7.23. A more complete analysis was precluded by the thermal instability of **3**.

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Registry No. 1, 99798-41-1; **2a**, 100228-64-6; **2b**, 100228-65-7; **2c**, 100228-66-8; **3**, 100228-67-9; $AlMe_2Cl$, 1184-58-3; 3,3-dimethylcyclopropene, 3907-06-0; Tebbe reagent, 67719-69-1; benzophenone, 119-61-9; 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene, 67731-48-0; 1,1,2-trimethylcyclopropane, 4127-45-1.

Isolation of Intermediates in the Water Gas Shift Reactions Catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$

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The water gas shift (WGS) reaction catalyzed by bis(2,2′-bipyridine)carbonylruthenium(II) complexes under mild conditions (70–150 °C; 3–20 kg/cm^2 of CO) has been investigated. Turnover numbers for the H_2 formation of about 500 in 20 h have been obtained in an aqueous KOH solution containing $[Ru(bpy)_2(CO)Cl](PF_6)$ (bpy = 2,2′-bipyridine) as a catalyst precursor. The solvolysis of $[Ru(bpy)_2(CO)Cl]^+$ in an aqueous solution affords $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, which exists as an equilibrium mixture with $[Ru(bpy)_2(CO)(OH)]^+$ in a weak alkaline solution. Coordinated H_2O of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ is readily substituted by CO to produce $[Ru(bpy)_2(CO)_2]^{2+}$, which undergoes a nucleophilic attack of OH^- to afford $[Ru(bpy)_2(CO)C(O)OH]^+$. This hydroxycarbonyl complex not only exists as an equilibrium mixture with $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)(COO^-)]^+$ in alkaline media but also undergoes a decarboxylation reaction at elevated temperatures to give CO_2 and $[Ru(bpy)_2(CO)H]^+$, which further reacts with H_3O^+ to evolve H_2 and regenerate $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. All these species involved in the cycle of the WGS reaction catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ have been isolated or characterized by spectrophotometry.

Introduction

Since the homogeneous water gas shift (WGS) reaction (eq 1) catalyzed by transition-metal complexes was reported in 1977,[1] a large number of homogeneous WGS reactions under mild conditions have been studied by

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$