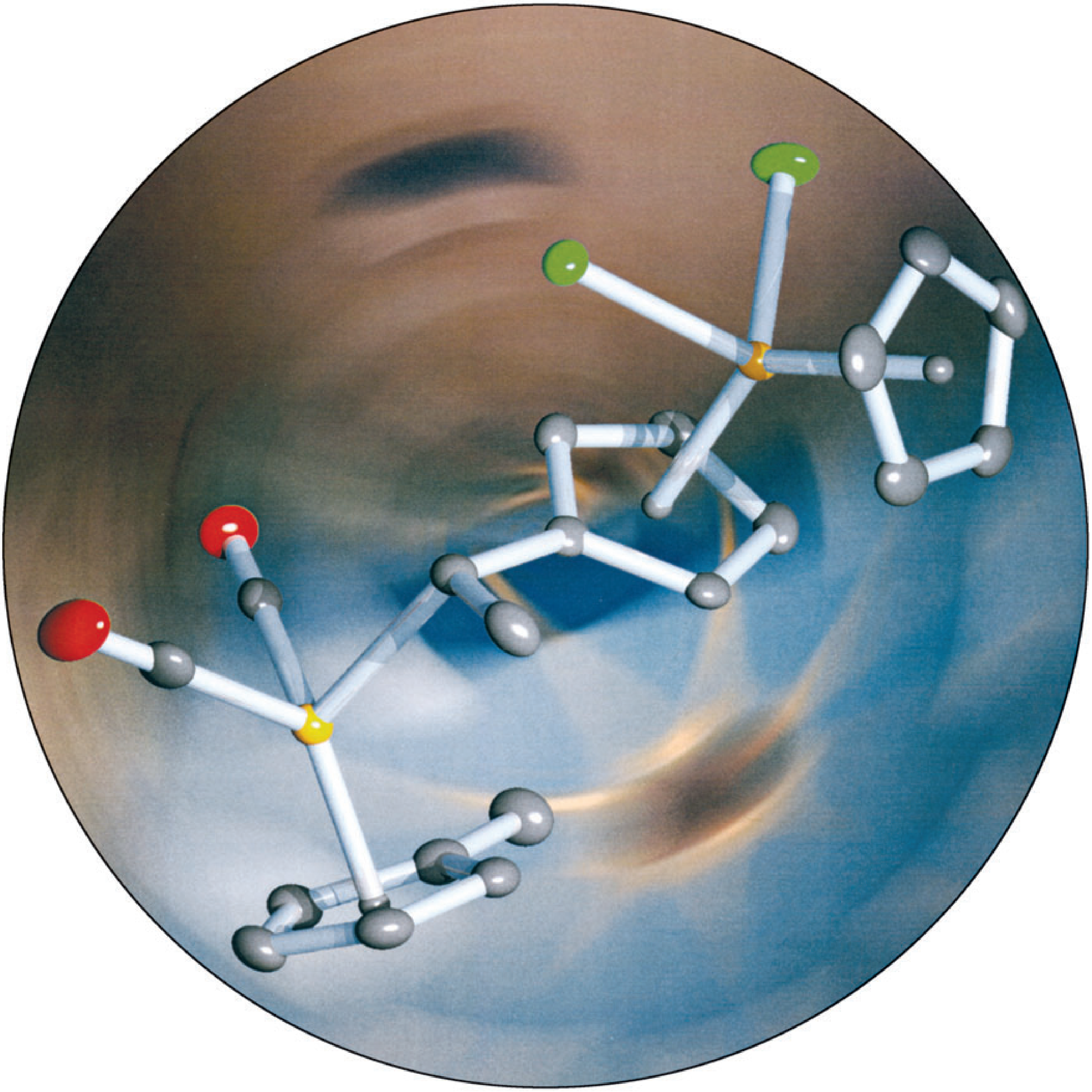
Zuschriften



Der abgebildete Komplex $[RuTi(\mu_2\text{-}\eta^1\text{-}\eta^5\text{-}CHMe(C_5H_4))(CO)_2(\eta\text{-}C_5H_4Me)(\eta\text{-}C_5H_5)Cl_2]$ entsteht bei der Behandlung eines Vorläufer-Metallocenkomplexes mit Säure. Diese C-C-Kupplung wurde bislang als unbekannt angesehen. Einzelheiten dazu finden Sie in der Zuschrift von G. A. Koutsantonis et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200500224

Metallocene Chemistry

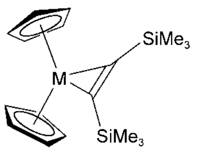
Reaction of Ruthenium Ethyne-1,2-diyl Compounds with Bis(trimethylsilyl)acetylene Complexes of Titanocene and Zirconocene: Remarkable Transfer of a C_2 Ligand**

Christopher S. Griffith, George A. Koutsantonis, Brian W. Skelton, and Allan H. White*

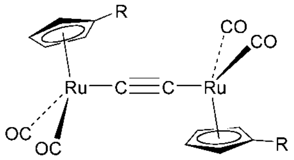
The chemistry of the metallocene bis(trimethylsilyl)alkyne complexes of Group 4 metals $[(\eta\text{-}C_5H_5)_2M\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ (**1**, M = Ti; **2**, M = Zr·(thf)) has been initiated and pursued by Rosenthal and co-workers for a considerable amount of time.[1] These complexes provide fragments that react readily with a variety of unsaturated compounds. Such fragments have unstable 14-electron configurations in which the two unoccupied orbitals and single occupied orbital of the metallocene units provide a plausible explanation for the diverse chemistry exhibited by these complexes, which often form metallacycles.[1–7]

We, in turn, have been interested in the use of substrates reactive to sites of unsaturation as building blocks for the rational preparation of larger molecules from ruthenium ethyne-1,2-diyl compounds,[8–16] and viewed complexes **1** and **2**[6] as excellent candidates for this purpose. Both complexes contain a ligand that stabilizes the reactive metal center, but which is easily removed to allow access to the reactivity of the unsaturated metal. The displacement of $Me_3SiC{\equiv}CSiMe_3$ from the metal coordination spheres of complexes **1** and **2** has been exploited by Rosenthal and co-workers with a range of diynes and polyynes.[3]

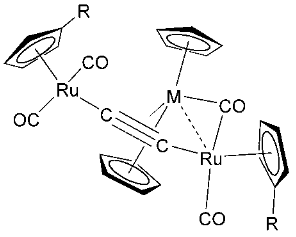
Herein we report the reaction of the ruthenium ethyne-1,2-diyl compounds $[\{Ru(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu\text{-}C_2)]$ (**3a**, R = H; **3b**, R = CH_3) with the reactive fragments "$(\eta\text{-}C_5H_5)_2M$" derived from **1** and **2**. These reactions proceeded at ambient temperatures in tetrahydrofuran to give excellent yields of the ethynediyl-coordinated metallocenes **4** and **5**. Direct in situ reaction with Group 4 metallocene dichloride and magnesium resulted in the recovery of the known compound $[RuCl(CO)_2(\eta\text{-}C_5H_5)]$ from other indeterminate products in moderate yield. The excess of complexes **1** and **2** was removed by simple hexane extraction, but no attempt was made to isolate the liberated $Me_3SiC{\equiv}CSiMe_3$. Similar reactions performed at 40–50 °C were essentially complete after ten hours with little or no decrease in yield of the complexes. Each complex exhibits similar infrared spectra with five $\nu(CO)$ absorptions, of which the absorption at $\approx 1730\ cm^{-1}$ was assigned to the bridging carbonyl ligand between the ruthenium and Group 4 metal centers. The ^1H NMR spectra of the three complexes display resonances of four magnetically inequivalent cyclopentadienyl groups. The two singlet resonances attributable to the metallocene fragment in each spectrum are significantly shifted between 1.06–1.25 ppm upfield from those of **1** or **2**. The two singlet resonances assigned to the $Ru(\eta\text{-}C_5H_5)$ moieties of **4a** and **5** are shifted with respect to that observed for **3a**, one 0.06–0.11 ppm upfield, and the other 0.35–0.30 ppm downfield. Similar changes in chemical shift values relative to those of **3b** are also observed for **4b**, with the methine ring resonances at lower field appearing as four resolved singlet resonances, and with the higher field resonances appearing as a virtual triplet. Two singlet resonances at $\delta = 1.98$ and $\delta = 1.67$ ppm are assigned to the methyl protons of the two C_5H_4Me rings. Complexes **4** and **5** are moderately air-sensitive in the solid state but more so in solution, and are best handled in an inert atmosphere.



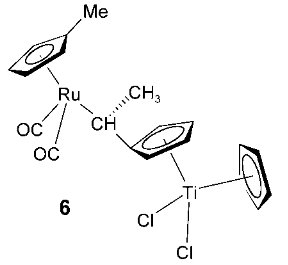
1: M = Ti
2: M = Zr • (thf)



3a: R = H
3b: R= Me



4a: M = Ti, R = H
4b: M = Ti, R= Me
5 : M = Zr, R = H



6

The ^{13}C NMR spectra measured for **4a** and **4b** contain resonances at $\delta \approx 106.0$ and $\delta \approx 105.0$ ppm, which are assigned to the titanocene moiety. The magnetic inequivalence of the $Ru(\eta\text{-}C_5H_4R)$ moieties is illustrated by the two singlet resonances at $\delta = 88.1$ and $\delta = 89.7$ ppm for **4a** and eight resolved singlet resonances at $\delta = 90.8$, 88.4, 88.0, 87.9, 86.3, 85.5, 85.3, and 85.1 ppm for **4b**. The two singlet resonances at $\delta = 114.4$ and 108.2 ppm are attributed to the *ipso* carbon atoms of the two C_5H_4Me rings. The two resonances present at ≈ 200 ppm for **4a** and **4b** are assigned to the two terminal carbonyl groups of the pendent $\{Ru(CO)_2(C_5H_4R)\}$ fragment on the basis of their chemical shifts. The resonances at $\delta =$ 203.9 and 204.4 ppm for **4a** and **4b**, respectively, are assigned to the remaining terminal carbonyl ligands coordinated to ruthenium. Downfield singlet resonances at $\delta = 305.5$ and 307.7 ppm in the spectra of **4a** and **4b**, respectively, are attributed to the bridging carbonyl group between the

---

[*] Dr. C. S. Griffith, Dr. G. A. Koutsantonis, Dr. B. W. Skelton, Prof. A. H. White
Chemistry, School of Chemical and Biomedical Sciences
University of Western Australia
35 Stirling Highway, Perth, WA, 6009 (Australia)
Fax: (+62) 8-6488-7247
E-mail: gak@chem.uwa.edu.au

[**] C.S.G. was the holder of an Australian Postgraduate Award.

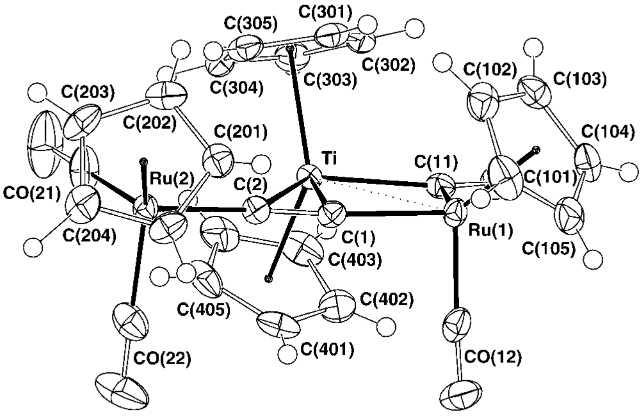


Figure 1. Molecular structure of **4a** (30% probability amplitude ellipsoids).

titanium and ruthenium centers on the evidence of related semibridging carbonyl groups of the early/late transition metal heterobimetallic complexes $[Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)Zr(\eta\text{-}C_5Me_5)_2]$[17] and $[Ru(CO)(\mu\text{-}C(O)CH_2CH_2\text{-}(\eta\text{-}C_5H_4))(\mu\text{-}CO)Zr(\eta\text{-}C_5H_5)_2]$.[18] The carbon atoms of the coordinated ethyne-1,2-diyl unit are assigned to resonances at $\delta = 167.6$ and 93.7 ppm for **4a** and $\delta = 167.0$ and 101.6 ppm for **4b**. The connectivity of **4a** (Figure 1)[19] was established by X-ray single-crystal structure determination, and demonstrates the formation of an alkyne adduct of essentially "$Ti(C_5H_5)_2$" not unlike that of the starting material **1**. The most striking difference is that the ethyne-1,2-diyl moiety is coordinated in an unsymmetrical η^2 fashion to a titanocene fragment with a symmetrical bridging carbonyl group between the titanium atom and one of the ruthenium atoms. The ruthenium, titanium, and the alkynyl carbon atoms of the coordinated ethyne-1,2-diyl ligand are not strictly coplanar, but for the purpose of describing the overall geometry and connectivity of **4a**, they may be regarded as such. The Cp_1-Ti-Cp_2 angle of 130.8° is similar to that measured in several metallocene η^2-alkyne solid-state structures.[20] Coordination of the ethyne-1,2-diyl ligand is significantly distorted from the ideal η^2 coordination as observed from the measured Ti−C(1) and Ti−C(2) distances of 2.230(2) and 2.546(2) Å, respectively, and from a projection onto the $TiRu_2C_2$ plane as well. The measured C(1)−C(2) bond length of 1.229(3) Å is close to that of complex **3a** (1.19 Å), which indicates that substantial triple-bond character remains, and that the metallacyclopropene structure found for metallocene η^2-alkyne complexes[20–22] is not an appropriate description of the bonding situation present in **4a**. The unsymmetrical coordination of the C≡C unit to the titanium atom appears to be a direct result of the μ_2-η^1-CO ligand bridging the Ti and Ru(1) metal atoms. The separation of 2.9670(5) Å between the Ru(1) and Ti atoms is significantly larger than the sum of the metallic radii (2.81 Å), so that the presence of metal–metal bonding can be questioned. However, the range of Ti–Ru distances found in crystallographically characterized complexes ranges from ≈2.56 Å in complexes that contain unsupported metal–metal bonds stabilized by a trisilylsilane-based tripodal amido ligand,[23] ≈2.66 Å in $[(Me_2N)_3Ti\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]$,[24,25] and a significantly longer distance of ≈2.93 Å found in $Ti_2Ru_2S_4$ cubane-type clusters.[26] In these latter complexes it is believed that the electron-rich Ru atom participates in a dative-style donation to the electron-poor Ti atom. This variation in bond distance implies some ambiguity, and thus we represent the bonding between Ti and Ru centers in complexes **4** as dative, being supported by the electronic contribution from the bridging carbonyl ligand.

We were interested in the reactivity of complexes **4** and consequently conducted some reactions of those complexes with both terminal and internal alkynes, but no transformations were observed. In a manner similar to $Me_3SiC{\equiv}CSiMe_3$, the sterically encumbered ethyne-1,2-diyl ligand appears to hinder further addition of alkyne moieties to the titanium metal center, although Rosenthal and co-workers have observed varied modes of reactivity.[1,2,6]

Complex **4a** did react with carbon monoxide to afford complete transformation of the starting material with both **3a** and $[Ti(CO)_2(\eta\text{-}C_5H_5)_2]$ isolated as products. Shur and co-workers[27,28] explored the reactivity of the tolane adduct of titanocene and found that protonation of the complex by HCl/EtOH afforded *cis*-stilbene and $[TiCl_2(\eta\text{-}C_5H_5)_2]$ in essentially quantitative yield. Rosenthal and co-workers found that the Cp* (η-C_5Me_5) and (η-C_5H_5) ligands influence the reactivity of titanocene and zirconocene alkyne complexes toward water.[29] We considered protonation as a possible route to the previously unobserved ethene-1,2-diyl complexes, M-C(H)=C(H)-M and (M = $Ru(CO)_2(\eta\text{-}C_5H_4R)$). Thus, dropwise addition of ethanolic HCl to a toluene solution of complex **4b** gave the new complex **6**. The red/purple residue that remains after hexane extraction can be recrystallized to give compound **6**, $[RuTi(\mu_2\text{-}\eta^1\text{-}\eta^5\text{-}CHMe(C_5H_4))(CO)_2(\eta\text{-}C_5H_4Me)(\eta\text{-}C_5H_5)Cl_2]$, in good yield. The hexane extract of the reaction mixture afforded a pale yellow carbonyl-containing compound that has yet to be identified. Complex **6** is moderately air-sensitive in the solid state but more so in solution, and is best handled in an inert atmosphere. The spectroscopic data is consistent with the presence of at least one $\{Ru(CO)_2(\eta\text{-}C_5H_4Me)\}$ fragment. A number of likely candidate complexes, $[RuH(CO)_2(\eta\text{-}C_5H_4Me)]$, $[RuCl(CO)_2(\eta\text{-}C_5H_4Me)]$, and $[Ru(C{\equiv}CH)(CO)_2(\eta\text{-}C_5H_4Me)]$ have been discounted on the basis of their infrared and ^1H NMR spectra. The spectroscopic data measured for **6** is consistent with the determined single-crystal structure. The ^1H NMR spectrum is complicated by multiplets that are attributed to the methine protons of the substituted cyclopentadienyl ligands coordinated to ruthenium (4.99–4.91 ppm) and titanium (6.61–6.09 ppm). A singlet resonance at $\delta = 6.46$ ppm is assigned to the unsubstituted cyclopentadienyl ligand of the titanocene fragment and appears in a ratio of 5:8 to the foregoing methine resonances. The nonmethyl proton of the (CH(Me)) unit appears as a quartet ($^3J = 6.8$ Hz) at $\delta = 4.12$ ppm from coupling to the adjacent methyl protons. A doublet centered at $\delta = 1.43$ ppm displays a corresponding ^3J-coupling constant of 6.8 Hz and is assigned to the methyl protons of (CH(Me)). A singlet resonance at $\delta = 1.97$ ppm is assigned to the methyl protons of the η-C_5H_4Me ligand. The ^{13}C NMR spectrum of **6** contains two downfield singlet resonances at $\delta = 202.6$ and

201.9 ppm, both assigned to the terminal carbonyl ligands of the $\{Ru(CO)_2(\eta\text{-}C_5H_4Me)\}$ fragment. Two singlet resonances at $\delta \approx 13.0$ ppm are attributed to the methyl groups of the η-C_5H_4Me ligand and (CH(Me)) unit. A singlet resonance at $\delta = 28.5$ ppm is assigned to the tertiary carbon of the (CH(Me)) unit. Resonances assigned to the ring carbon atoms of $Ru(\eta\text{-}C_5H_4Me)$ appear as four singlets between 89.9 and 88.3 ppm with a weak resonance at $\delta = 108.7$ ppm, tentatively assigned to the *ipso* carbon atom of the η-C_5H_4Me ligand. The unsubstituted η-C_5H_5 ligand of the metallocene fragment appears as a singlet resonance at $\delta = 119.4$ ppm with four singlet resonances between 126.8 and 110.4 ppm assigned to $Ti(\eta\text{-}C_5H_4)$. The corresponding *ipso* carbon gives rise to an unusual downfield singlet resonance at $\delta = 160.0$ ppm.

The structure of **6** (Figure 2)[30] is best described as a monosubstituted cyclopentadienyl titanocene dichloride fragment with a pendent $\{Ru(CHMe)(CO)_2(\eta\text{-}C_5H_4Me)\}$ group.

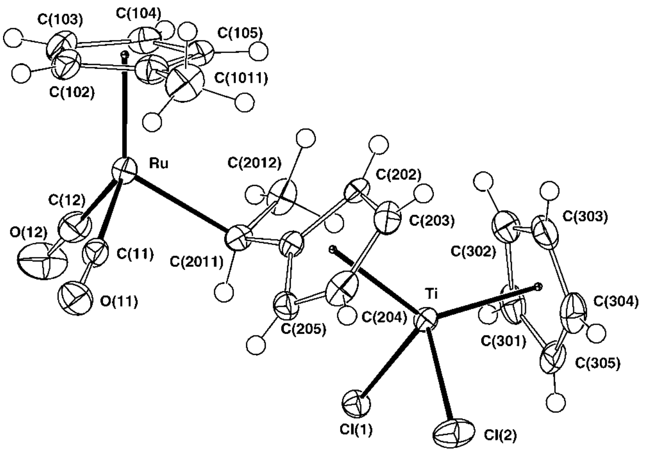
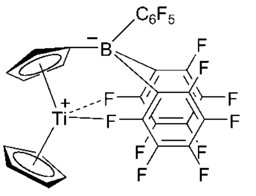


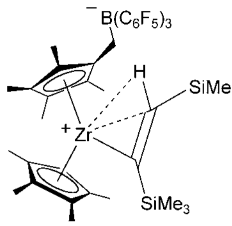
Figure 2. Molecular structure of **6** (30% probability amplitude ellipsoids).

The geometry about the titanium atom is unremarkable in comparison with $[TiCl_2(\eta\text{-}C_5H_5)_2]$,[31] and the geometry about the ruthenium atom is also a typical "piano stool". The measured bond length of 2.199(5) Å for Ru–C(2011) is significantly elongated from the Ru–C(sp) bond length of 2.055(2) Å for **3b**, but compares well with the average value of 2.18 Å found for the alkyl bridged diruthenium complexes, $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}(\mu\text{-}(CH_2)_x)]$ ($x = 1$,[32] $x = 2$,[33] $x = 5$[34]), which implies sp^3 hybridization at C(2011). This observation is supported by the C(2011)–C(2012) distance of 1.526(5) Å which is similar to other C–C (sp^3) single bond lengths and a tetrahedral geometry about C(2011). The carbon atom (C(2011)) that bridges the ruthenium and C(201) atoms is essentially coplanar with the cyclopentadienyl ring carbon atoms (C201–205) of the titanocene dichloride fragment with a measured C(2011)–C(201) distance of 1.493(5) Å, similar to the value of 1.503(6) Å determined for C(1011)–C(101) bond distance of the methyl-substituted cyclopentadienyl ring.

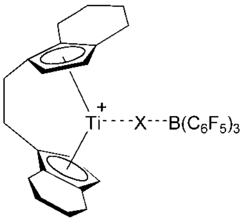
We believe that the formation of **6** is unprecedented. A close examination of the connectivity reveals the apparent transfer of the now fully protonated C_2 unit found in **4b** (originally bound in an η^2 fashion to Ti and η^1 to the two ruthenium atoms) to a $Ti(\eta\text{-}C_5H_5)$ unit. Low-valence Group 4 permethyl cyclopentadienide complexes have afforded reactivity at the $(\eta\text{-}C_5Me_5)$ ring by C–H activation.[35] Formation of the $\{(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)TiCl_2\}$ fragment is also not unexpected given that the protonation of the tolane adduct of titanocene gave titanocene dichloride as a product of the reaction.[27,28] The mass balance in the reaction is essentially satisfied in the yield of **6** (Ti) and presumably with the remaining ruthenium found in the unidentified complex. Given that this other product remains unidentified, any meaningful speculation on a mechanism for the formation of **6** is difficult, but it is tempting to consider that it results from the multiple protonation of the C≡C unit of complex **4b** to give the $(\mu^2\text{-}\eta^1{:}\eta^5\text{-}C(H)(CH_3)(C_5H_4))$ ligand bridging the two metal centers with concomitant oxidation of the titanium center. At this stage, we cannot discount the insertion of ethene derived from the dehydration of EtOH. Complex **4b** does not react with ethene and is also unreactive toward water, suggesting that reaction with EtOH is also unlikely. There are other observations made by Rosenthal and coworkers in their seminal contributions, reviewed recently,[1,6] that are relevant to the discussion of a possible mechanism. First, in the reaction of **1** with $B(C_6F_5)_3$ a zwitterionic complex, **7**, containing the $B(C_6F_5)_3$ bound to the $(\eta\text{-}C_5H_5)$ ring was observed with the elimination of hydrogen, 1,2-bis(trimethylsilyl)acetylene, and importantly, 1,2-bis(trimethylsilyl)ethane. Other alkyne adducts of titanocene gave identical products. Second, in the analogous reaction of $[(\eta\text{-}C_5Me_5)_2Zr(Me_3SiC{\equiv}CSiMe_3)]$ with $B(C_6F_5)_3$ there was no hydrogen or alkyne liberated; rather, the zwitterionic Zr^{IV} derivative, **8**, containing a σ-alkenyl ligand was isolated. Finally, the bis(trimethylsilyl)acetylene complex of *rac*-1,2-ethylene-1,1-bis(η^5-tetrahydroindenyl)titanium reacted with the Brønsted acid $B(C_6F_5)_3{\cdot}H_2O$ to give a mixture of complexes **9** and **10**. Literature precedent[36] allows the formulation of a relatively simple mechanism in which the



7



8



9: X = H
10: X = OH

η^2-bound ethynediyl complex rearranges to form a bridging $TiRu(\mu\text{-}\eta^1\text{-}C{\equiv}C\text{-}Ru(CO)_2(\eta\text{-}C_5H_4R))$ moiety. Subsequent hydrogen elimination from a $Ti(\eta\text{-}C_5H_5)$ group leads to the formation of a bridging (μ-η^1:η^5) cyclopentadienyl ligand between the Ru and Ti atoms. Such structures are typical in organometallic chemistry and are formed by C–C homocoupling of 1,3-butadiyne and fulvene ligands. Acetylide coupling reactions[3,7,37] and cyclopentadienyl coupling reactions[6,21] are well-known in the literature. Analogous mixed heterocoupling would give either a Ru–CC–Cp unit or Ru–C(=C)–Cp intermediates, which, upon reaction with acid of the latter, lead to the observed Ru–CH(Me)–Cp moiety in **6**. Presumably, the known mobility of the C_2 group,[8,37] which we have described as bearing-like, causes discrimination between the preferred Ru–C(=C)–Cp compound over that of the Ru–CC–Cp and of Ru–CH(Me)–Cp over that of $Ru\text{–}CH_2CH_2\text{–}Cp$.

In spite of these observations, however, it still remains difficult to differentiate intermolecular protonation from intramolecular C–H activation. We are currently undertaking detailed isotope labeling studies that will ultimately shed light on the mechanism of formation of **6**.

In conclusion, we have compared the reactivity of our metalloalkynes, (the ruthenium ethyne-1,2-diyl complexes **3**) with that of the bulky 1,2-bis(trimethylsilyl)acetylene and found that upon coordination to titanocene, they have similar reactivity. However, upon reaction with acid, we have observed what appears to be an unprecedented transformation to give a ruthenium hydrocarbyl complex attached to titanocene dichloride. We are making a detailed examination of the reactivity of **6**, particularly with respect to its efficacy as a catalyst for the polymerization of 1-alkenes.

Experimental Section

The manipulation of oxygen- and moisture-sensitive compounds was performed under an atmosphere of high-purity argon with standard Schlenk techniques or in a dry box (Miller Howe). Infrared spectra were recorded with a Bio-Rad FTS 45 and 40 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were acquired with Varian Gemini 200 and Bruker ARX 500 spectrometers. ^{31}P NMR spectra were acquired with a Bruker ARX 500 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced with respect to incompletely deuterated solvent signals. Mass spectra were obtained on a VG AutoSpec spectrometer employing a FAB ionization source in all samples unless otherwise specified. Elemental analyses were performed at The Research School of Chemistry Microanalytical Unit, Australian National University, ACT. Tetrahydrofuran was dried over sodium metal and distilled from potassium benzophenone ketyl under an atmosphere of argon. Hexanes and toluene were dried over sodium metal and distilled under an atmosphere of argon. Distilled solvents were stored over sodium or potassium mirrors until use.

4a: A solution of $[Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)_2]$ (**1**; 42 mg, 0.121 mmol) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu_2\text{-}C{\equiv}C)]$ (**3a**; 50 mg, 0.107 mmol) in THF (20 mL) was stirred for 10 h at 50 °C. The solvent was removed in vacuo, and the dark residue was washed with *n*-hexanes (2 × 20 mL) to remove $Me_3SiC{\equiv}CSiMe_3$. Recrystallization (toluene/*n*-hexanes, −40 °C) gave dark red platelets of **4a** (58 mg, 84 %). IR (THF): $\tilde{\nu}_{CO} = 2032$s, 1977s, 1931s, 1907w, 1733s cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 5.36$ (s, 5 H, C_5H_5Ti), 5.20 (s, 5 H, C_5H_5Ti), 4.98 (s, 5 H, C_5H_5Ru), 4.53 ppm (s, 5 H, C_5H_5Ru); ^{13}C NMR (C_6D_6): $\delta = 305.5$ (s, μ-CO), 203.9 (s, CO), 199.5 (s, CO), 199.2 (s, CO), 167.6 (s, $(Ti)Ru\mathit{C}{\equiv}C$), 106.4 (s, C_5H_5Ti), 105.1 (s, C_5H_5Ti), 93.7 (s, $C{\equiv}\mathit{C}Ru(CO)_2(C_5H_5)$), 89.7 (s, C_5H_5Ru), 88.1 ppm (s, C_5H_5Ru); elemental analysis: calcd. for $C_{26}H_{20}O_4Ru_2Ti_1$: C 48.29, H 3.12; found: C 48.19, H 2.96.

4b: A solution of $[Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)_2]$ (**1**; 87 mg, 0.250 mmol) and $[\{Ru(CO)_2(\eta\text{-}C_5H_4Me)\}_2(\mu_2\text{-}C{\equiv}C)]$ (**3b**; 100 mg, 0.200 mmol) in THF (30 mL) was stirred for 10 h at 50 °C. The solvent was removed in vacuo, and the dark residue was washed with *n*-hexanes (2 × 20 mL) to remove $Me_3SiC{\equiv}CSiMe_3$. Recrystallization (toluene/*n*-hexanes, −40 °C sol. diff.) gave dark red crystals of **4b** (119 mg, 88 %). IR (THF): $\tilde{\nu}_{CO} = 2035$s, 1980s, 1934s, 1907w, 1735s cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 5.39$ (s, 5 H, C_5H_5Ti), 5.24 (s, 5 H, C_5H_5Ti), 4.96 (s, 1 H, $C_5\mathit{H}_4Me$), 4.87 (s, 1 H, $C_5\mathit{H}_4Me$), 4.84 (s, 1 H, $C_5\mathit{H}_4Me$), 4.73 (s, 1 H, $C_5\mathit{H}_4Me$), 4.45 (s, 1 H, $C_5\mathit{H}_4Me$), 4.41 (s, 2 H, $C_5\mathit{H}_4Me$), 4.37 (s, 1 H, $C_5\mathit{H}_4Me$), 1.98 (s, 3 H, $C_5H_4\mathit{Me}$), 1.67 ppm (s, 3 H, $C_5H_4\mathit{Me}$); ^{13}C NMR (C_6D_6): $\delta = 307.7$ (s, μ-CO), 204.4 (s, CO), 199.8 (s, CO), 199.6 (s, CO), 167.0 (s, $(Ti)Ru\mathit{C}{\equiv}C$), 114.4 (s, *ipso*-C), 108.2 (s, *ipso*-C), 106.5 (s, C_5H_5Ti), 105.0 (s, C_5H_5Ti), 101.6 (s, $C{\equiv}\mathit{C}Ru(CO)_2(C_5H_5)$), 90.8 (s, C_5H_4Me), 88.4 (s, C_5H_4Me), 88.0 (s, C_5H_4Me), 87.9 (s, C_5H_4Me), 86.8 (s, C_5H_4Me), 85.5 (s, C_5H_4Me), 85.3 (s, C_5H_4Me), 85.1 (s, C_5H_4Me), 14.0 (s, $C_5H_4\mathit{Me}$), 13.7 ppm (s, $C_5H_4\mathit{Me}$); elemental analysis: calcd. for $C_{28}H_{24}O_4Ru_2Ti_1$: C 49.86, H 3.59; found: C 49.68, H 3.56.

5: A solution of $[Zr(thf)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)_2]$ (**2**; 52 mg, 0.133 mmol) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu_2\text{-}C{\equiv}C)]$ (**3a**; 50 mg, 0.107 mmol) in THF (20 mL) was stirred for 48 h at ambient temperature. The solvent was removed in vacuo and the orange residue was washed with *n*-hexanes (2 × 20 mL) to remove $Me_3SiC{\equiv}CSiMe_3$. Recrystallization (THF/*n*-hexane) gave an orange powder of **5** (38 mg, 55 %). IR (toluene): $\tilde{\nu}_{CO} = 2039$s, 1978s, 1938s, 1909w, 1729s cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 5.51$ (s, 5 H, C_5H_5Zr), 5.36 (s, 5 H, C_5H_5Zr), 4.93 (s, 5 H, $C_5H_5Ru(Zr)$), 4.58 ppm (s, 5 H, $C_5H_5Ru(Zr)$). The spectroscopic properties of **5** are similar to those of the Ti analogue **4a** with no indication of any other species present.

6: To a solution of $[Ru_2Ti(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_4Me)_2(\eta\text{-}C_5H_5)_2]$ (**4b**; 15 mg, 0.22 mmol) in toluene (10 mL) a solution of HCl/(EtOH) (0.5 mL, ≈0.006 g mL^{-1}) was added dropwise to give an immediate color change from dark to pale red. The reaction mixture was stirred for 30 min, followed by solvent removal in vacuo. The residues were washed with *n*-hexanes (50 mL) to give a yellow solution. Removal of the solvent in vacuo afforded a yellow crystalline compound, which remains unidentified (8 mg). IR (toluene): $\tilde{\nu}_{CO} = 2022$s, 1995s cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 4.50$ (m, 1 H), 4.19 (t, 4 H), 3.92 (t, 4 H), 1.46 ppm (s, 6 H); ^{13}C NMR (C_6D_6): $\delta = 197.6$ (s, CO), 119.3 (s), 88.8 (s), 88.6 (s), 83.6 (s), 82.4 (s), 12.7 ppm (s); elemental analysis: found: C 38.67, H 3.48. Extraction of the remaining residues with diethyl ether (30 mL) and subsequent recrystallization (CH_2Cl_2/*n*-hexanes) gave purple rods of **6** (10 mg, 90 % with respect to Ti). IR (toluene): $\tilde{\nu}_{CO} = 2010$s, 1957s cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 6.61$ (m, 1 H, C_5H_4Ti), 6.46 (s, 5 H, C_5H_5), 6.22 (m, 1 H, C_5H_4Ti), 6.17 (m, 1 H, C_5H_4Ti), 6.09 (m, 1 H, C_5H_4Ti), 4.99–4.91 (m, 4 H, $C_5\mathit{H}_4Me$), 4.12 (q, $^3J = 6.8$ Hz, 1 H, $C\mathit{H}Me$), 1.97 (s, 3 H, $C_5H_4\mathit{Me}$), 1.43 ppm (d $^3J = 6.8$ Hz, 3 H, $CH\mathit{Me}$); ^{13}C NMR (CD_2Cl_2): $\delta = 202.6$ (s, CO), 201.9 (s, CO), 160.0 (s, *ipso*-C(Ti)), 126.8 (s, C_5H_4Ti), 119.4 (s, unsubst. C_5H_4Ti), 110.8 (s, C_5H_4Ti), 110.4 (s, C_5H_4Ti), 108.7 (s, *ipso*-C(Ru)), 89.9 (s, C_5H_4Me), 89.4 (s, C_5H_4Me), 88.9 (s, C_5H_4Me), 88.3 (s, C_5H_4Me), 28.5 (s, $\mathit{C}HMe$), 13.4, 12.7 ppm (2 × s, $C_5H_4\mathit{Me}$ and $CH(\mathit{Me})$); MS (FAB) $[M-(Ti(CO)(C_5H_5)Cl_2)]^+$ $m/z = 303$ (100 %); experimental analysis: calcd. for $C_{20}H_{20}Cl_2O_2RuTi$: C 46.89, H 3.94; found: C 47.32, H 3.92.

Received: January 20, 2005

Keywords: cyclopentadienyl ligands · metallocenes · ruthenium · titanium · zirconium

[1] U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, V. B. Shur, *Eur. J. Inorg. Chem.* **2004**, 4739 – 4749.

[2] A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burkalov, U. Rosenthal, *Synlett* **1996**, 111 – 118.

[3] U. Rosenthal, P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, *Acc. Chem. Res.* **2000**, *33*, 119 – 129.

[4] U. Rosenthal, V. V. Burlakov, *Titanium Zirconium Org. Synth.* **2002**, 355 – 389.

[5] U. Rosenthal, P. Arndt, W. Baumann, V. V. Burlakov, A. Spannenberg, *J. Organomet. Chem.* **2003**, *670*, 84 – 96.

[6] U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884 – 900.

[7] U. Rosenthal, *Angew. Chem.* **2004**, *116*, 3972 – 3977; *Angew. Chem. Int. Ed.* **2004**, *43*, 3882 – 3887.

[8] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Chem. Commun.* **2002**, 2174 – 2175.

[9] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2003**, *672*, 17 – 21.

[10] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2003**, *670*, 198 – 204.

[11] L. T. Byrne, J. P. Hos, G. A. Koutsantonis, V. Sanford, B. W. Skelton, A. H. White, *Organometallics* **2002**, *21*, 3147 – 3156.

[12] L. T. Byrne, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *598*, 28 – 35.

[13] L. T. Byrne, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1999**, *592*, 95 – 102.

[14] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Chem. Commun.* **1998**, *7*, 1805 – 1806.

[15] L. T. Byrne, C. S. Griffith, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 259 – 265.

[16] L. T. Byrne, C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1998**, 1575 – 1580.

[17] P. T. Barger, J. E. Bercaw, *Organometallics* **1984**, *3*, 278.

[18] C. P. Casey, R. E. Palermo, *J. Am. Chem. Soc.* **1986**, *108*, 549.

[19] **4a:** $C_{26}H_{20}O_4Ru_2Ti$; crystal dimensions: $0.65 \times 0.35 \times 0.15$ mm^3; $M = 646.5$ monoclinic, space group $P2_1/c$, $a = 11.157(1)$, $b = 17.182(2)$, $c = 12.698(2)$ Å, $\beta = 93.880(2)°$, $V = 2429$ Å^3, $Z = 4$, $\rho_{calcd} = 1.76(8)$ g cm^{-3}, $\mu_{Mo} = 15.8$ cm^{-1}; $T_{min/max} = 0.68$ (multiscan correction); $2\theta_{max} = 58°$; $N_{total} = 27124$ reflections (full sphere CCD data, monochromatic $Mo_{K\alpha}$ radiation, $\lambda = 0.7107(3)$ Å, $T \approx 153$ K) merging to $N_{unique} = 6082$ reflections ($R_{int} = 0.027$), $N_{obs} = 5334$ ($F > 4\sigma(F)$); $R = 0.026$, $R_w = 0.034$ (weights: $(\sigma^2(F) + 0.0004 F^2)^{-1}$); $(x,y,z,U_{iso})_H$ refined throughout. CCDC-261179 (**4a**) and CCDC-261180 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal, H. Goerls, *J. Organomet. Chem.* **1994**, *476*, 197 – 206.

[21] U. Rosenthal, A. Ohff, M. Michalik, H. Goerls, V. V. Burlakov, V. B. Shur, *Angew. Chem.* **1993**, *105*, 1228 – 1230; *Angew. Chem.* **1993**, *31*, 1193 – 1195.

[22] C. Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov, U. Rosenthal, *J. Organomet. Chem.* **1995**, *501*, 189 – 194.

[23] L. Gade, M. Schubart, B. Findeis, S. Fabre, I. Bezougli, M. Lutz, I. J. Scowen, M. McPartlin, *Inorg. Chem.* **1999**, *38*, 5282 – 5294.

[24] W. J. Sartain, J. P. Selegue, *Organometallics* **1989**, *8*, 2153 – 2158.

[25] W. J. Sartain, J. P. Selegue, *J. Am. Chem. Soc.* **1985**, *107*, 5818 – 5820.

[26] S. Kabashima, S. Kuwata, M. Hidai, *J. Am. Chem. Soc.* **1999**, *121*, 7387 – 7845.

[27] V. B. Shur, S. Z. Bernadyuk, V. V. Burlakov, V. G. Andrianov, A. I. Yanovskii, Y. T. Struchkov, M. E. Vol'pin, *J. Organomet. Chem.* **1983**, *243*, 157 – 163.

[28] V. B. Shur, V. V. Burlakov, M. E. Vol'pin, *J. Organomet. Chem.* **1988**, *347*, 77 – 83.

[29] P.-M. Pellny, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *Z. Anorg. Allg. Chem.* **1999**, *625*, 910 – 918.

[30] **6** (see Ref. [19] for general details) **:** $C_{20}H_{20}Cl_2O_2RuTi$, crystal dimensions: $0.30 \times 0.08 \times 0.06$ mm^3; $M = 512.2$ monoclinic, space group $C2/c$, $a = 31.391(4)$, $b = 6.6889(9)$, $c = 20.863(3)$ Å, $\beta = 116.306(2)°$, $V = 3927$ Å^3, $Z = 8$ $\rho_{calcd} = 1.73(3)$ g cm^{-3}, $\mu_{Mo} = 14.6$ cm^{-1}; $T_{min/max} = 0.79$; $2\theta_{max} = 58°$; $N_{total} = 23281$, $N_{unique} = 4988$ ($R_{int} = 0.063$), $N_{obs} = 3634$; $R = 0.038$, $R_w = 0.039$.

[31] A. Clearfield, D. K. Warner, C. H. Saldarringa-Molina, R. Ropal, I. Bernal, *Can. J. Chem.* **1975**, *53*, 1622.

[32] Y. C. Lin, J. C. Calabrese, S. S. Wreford, *J. Am. Chem. Soc.* **1983**, *105*, 1679.

[33] M. A. Gafoor, A. T. Hutton, J. R. Moss, *J. Organomet. Chem.* **1996**, *510*, 233.

[34] K. P. Finch, J. R. Moss, M. L. Niven, *Inorg. Chim. Acta* **1989**, *166*, 181.

[35] M. Horacek, P. Stepnicka, R. Gyepes, I. Cisarova, M. Polasek, K. Mach, P.-M. Pellny, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *J. Am. Chem. Soc.* **1999**, *121*, 10638 – 10639.

[36] We thank Professor Uwe Rosenthal for his insightful discussion and a reviewer for helpful comments.

[37] U. Rosenthal, *Angew. Chem.* **2003**, *115*, 1838 – 1842; *Angew. Chem. Int. Ed.* **2003**, *42*, 1794 – 1798.