Synthesis, Structure, and Reactions of Heterobinuclear μ-Methylene Complexes

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Sources of the reactive fragment $Cp_2Ti{=}CH_2$ react with a variety of late-transition-metal complexes containing μ-halides $[Cl-ML_n]_2$ to yield early–late binuclear complexes containing μ-CH_2, and μ-Cl ligands. Complexes containing Rh, Ir, Pt, Pd, and Au have been prepared and characterized. The X-ray structure of the complex $Cp_2Ti-CH_2-RhCl(COD)$ (COD = 1,5-cyclooctadiene) prepared from $Cp_2Ti-CH_2C(CH_3)_2-CH_2$ and $[Cl-Rh(COD)]_2$ has been determined. Crystallographic data: space group *Pbcm*; $Z = 4$; $a = 8.268$ (2) Å, $b = 16.409$ (4) Å, $c = 12.604$ (3) Å; $V = 1710$ (1) Å^3. The structure was refined to a final R of 0.069 and $R_{3\sigma}$ of 0.048 for the 1061 reflections that had $F_o > 3\sigma(F_o)$.

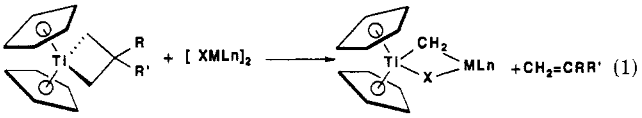
Introduction

Key intermediates in heterogeneous Fischer–Tropsch chemistry are μ-methylene species. There is growing evidence that reactions using noble metals supported on reducible metal oxides produce methylenes that bridge between the support metal centers and the supported metal. For example, titanium–rhodium bridged species have recently been proposed as intermediates in reactions over rhodium on titanium oxide supports.[1] Such species may be the key to understanding "strong metal support interactions", a dominant theme in heterogeneous catalysis.

Over the past few years a number of sources of the reactive fragment $Cp_2Ti{=}CH_2$ have been developed. This species will react with a variety of Lewis acids to yield adducts.[2] As indicated below this titanium reagent will react with a variety of transition-metal halides to yield models for μ-methylenes of the type proposed in strong metal-support interactions.[3]

Results and Discussion

Synthesis. A series of μ-CH_2 early–late heterobimetallic complexes have been prepared by reaction of bis(cyclopentadienyl)titanacyclobutanes[2] with late-transition-metal chloride and methoxide complexes (eq 1): the reaction appears to be general and leads to a series of products of variable stability and reactivities. Compounds **3a–d** have been isolated in 70–80% yields as crystalline, air-sensitive solids and were fully characterized. Compounds **3e–h** have only been observed spectroscopically. These are included to demonstrate generality (see Experimental Section). Compounds **3a**, **3b**, **3c**, and **3e** are thermally robust and are unaffected by extended heating in benzene at 65 °C. In contrast, **3g** decomposes within hours at 25 °C (to give paramagnetic products) and **3d** and **3f** decompose over a period of days at 25 °C (vide infra). It has also been shown that anion metathesis of the corresponding μ-Cl ligand with MeLi or MeMgX provides a generl entry to the μ-CH_2, μ-CH_3 complexes of type **3i**.[4]



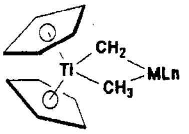
1 a-c 2 a-h 3 a-h

1a, R = Me, R′ = Me; R = Me, R′ = Pr; R = C(CH$_3$)$_3$, R′ = H; **2**,**3a**, ClRh(1,5-COD); **2**,**3b**, (MeO)Rh(1,5-COD); **2**,**3c**, ClIr(1,5-COD); **2**,**3d**, ClPd(2-methylallyl); **2**,3e, ClPt(Me)(SMe$_2$)$_n$ (**2**, n = 2; **3**, n = 1); **2**,**3f**, ClAu(PMe$_3$); **2**,**3g**, ClRh(CO)(SMe$_2$)$_n$ (**2**, n = 2; **3**, n = 1); **2**,**3h**, ClRh(C$_2$H$_4$)(SMe$_2$)$_n$ (**2**, n = 2; 3, n = 1) (1,5-COD = 1,5-cyclooctadiene)

Table I. ^{1}H and ^{13}C NMR Spectroscopic Data for the Bridging Methylene Compounds[a,b]

	chemical shifts in ppm relative to TMS	
compd	^{1}H	^{13}C
3a	7.48	186.5 ($^1J_{C-H}$ = 128 Hz, $^1J_{C-Rh}$ = 20 Hz)
3b	7.21	
3c	7.95	180.7 ($^1J_{C-H}$ = 132 Hz)
3d	8.17 (AB quartet) 7.90 ($^2J_{H-H}$ = 7.3 Hz)	
3e	7.42 ($^2J_{Pt-H}$ = 46.9 Hz)	152.7 ($^1J_{C-H}$ = 136 Hz, $^1J_{Pt-C}$ = 580 Hz)
	(Pt–Me) 1.09 ($^2J_{Pt-H}$ = 93.3 Hz)	–12.0 ($^1J_{C-H}$ = 130 Hz, $^1J_{Pt-C}$ = 855 Hz)
3f	6.91 ($^3J_{P-H}$ = 5.4 Hz)	
3g	7.48	
3h	6.77	

[a] See Experimental Section for full listing. [b] All data are for C$_6$D$_6$ solutions.



3i

Spectroscopic Data. Characteristically,[5] low-field ^{1}H and ^{13}C NMR signals are observed for the μ-CH_2 group (Table I). Assignment of the cis/trans isomerism at Pt in compound **3e** was made on the basis of NOE experiments. These showed that irradiation of the μ-CH_2 resonance caused enhancement of the Pt–Me resonance and vice versa. No NOE interaction was observed between the SMe$_2$ ligand and the Pt–Me or μ-CH_2 groups. It is therefore concluded that the μ-CH_2 and Pt–Me groups are cis to one another.

[†] Contribution no. 7671.

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(4) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402.

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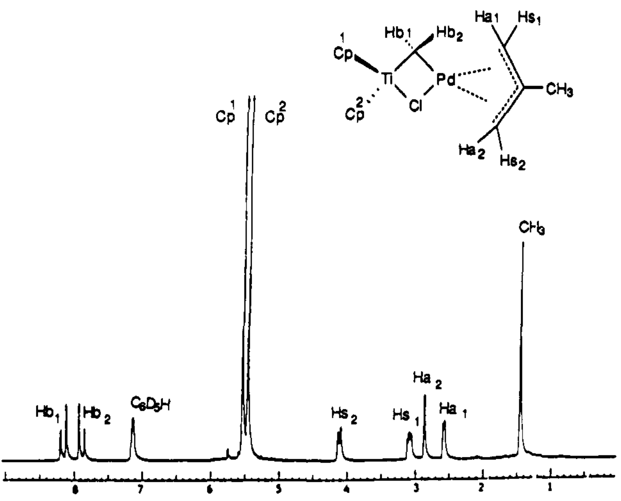
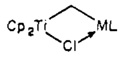


Figure 1. The 90-MHz ^1H NMR spectrum of **3d** in C_6D_6.

In the case of the (π-allyl)Pd complex **3d**, the spectral assignments shown in Figure 1 were made on the basis of homonuclear decoupling and NOE experiments, the results of which are unambiguous (see Experimental Section).

Coupling constants are of use in the determination of molecular structure and hybridization of CH_2 structures. In this case it is interesting to examine the various spin–spin coupling for compounds **3a–c** to determine if a choice can be made between the possible formal bonding structures represented by I and II. In the structure I the μ-carbon is sp^3 hybridized while in II it is sp^2. As models, the J_{CH} of the methyl group in a series of titanocene methyl complexes is 129 ± 5 Hz, while the J_{CH} of the methylidene ligand in the best model for II, $Cp_2Ti{=}CH_2{\cdot}PMe_3$, is 127 Hz.[6] It is obvious that J_{CH} is not a good indicator of hybridization in these systems.

Analysis of the J_{PtC} in **3e** is more informative. Any spin–spin couplings transmitted through the Pt–CH_2 bond should exhibit lower coupling constants if there is significant π bonding as in II than would obtain if the carbon orbital bonded to Pt was a pure sp^3 hybrid.[7] The coupling constants observed for the Pt–Me complex **3e** are consistent with the C orbital of the methylene used to bond to Pt having less s character than an sp^3 orbital, in that both $^1J_{Pt-C}$ (580 vs 855 Hz) and $^2J_{Pt-H}$ (47 vs 93 Hz) are higher for the Pt–Me group than for the μ-CH_2 group (Table I). Since the nature of the trans ligand is known to affect $^1J_{Pt-C}$ and $^2J_{Pt-H}$,[8] it is pertinent to note that the two trans ligands in this case, SMe_2 and μ-Cl, are expected to exert very similar trans influences. This expectation is based upon the reported observation of similar $^2J_{Pt-H}$ values for Pt–Me groups trans to SMe_2, μ-I, I, and Cl, all of which exhibit $^2J_{Pt-H}$ values in the range of 76–81 Hz.[9] The coupling constant data are thus consistent with a bonding description which is intermediate between those of structures I and II.



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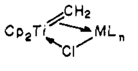

II

Table II. Crystal Data and Data Collection Information

formula	$TiRhC_{19}H_{24}Cl$
fw	438.66
space group	*Pbcm* (D_{2h}^{11}), No. 57
a, Å	8.268 (2)
b, Å	16.409 (4)
c, Å	12.604 (3)
V, Å³	1710 (1)
Z	4
λ, Å	0.71073
μ, mm⁻¹	9.19
cryst size, mm	0.046 × 0.333 × 0.442
D_{calcd}, g/mL	1.704
scans	θ–2θ; 2.4° in 2θ plus dispersn
reflctns	4 < 2θ < 50°; ± *h*,+*k*,±*l*
bdgd time/scan time	0.5
collected	6814 reflectns
averaged	1568 reflectns
final no. of parameters	114
secondary extinctn	2.95×10^{-7}
final cycle	
R	0.069 (1425[a])
$R_{3\sigma}$	0.048 (1061)
S	3.00 (1568)

[a] The number of reflections contributing to sums in parentheses.

Table III. Fractional Atomic Coordinates (×10⁵) and U_{eq}'s (×10⁴) or *B*'s

atom	*x*	*y*	*z*	U_{eq}, Å²
Rh	15178 (9)	23967 (4)	1/4	394 (2)
Ti	39981 (19)	37193 (9)	1/4	324 (4)
Cla[a]	9939 (54)	38390 (26)	1/4	484 (16)
Clb[a]	44401 (65)	22355 (31)	1/4	622 (17)
Cp1	34294 (100)	44119 (44)	8649 (54)	560 (22)
Cp2	47521 (105)	47869 (41)	13085 (63)	560 (23)
Cp3	59887 (88)	42142 (55)	13067 (61)	624 (26)
Cp4	54506 (99)	34832 (50)	8999 (61)	591 (24)
Cp5	38381 (97)	36041 (46)	6236 (56)	585 (25)
C81	15373 (83)	11595 (36)	19717 (54)	526 (18)
C82	967 (103)	9735 (59)	12989 (78)	900 (30)
C84	−9541 (89)	22978 (51)	19381 (89)	1098 (34)
atom	***x***	***y***	***z***	***B***
C83a[a]	−815 (24)	1608 (12)	995 (17)	6.5 (5)
C83b[a]	−1427 (22)	1501 (10)	1617 (15)	5.9 (4)
C1a[a]	4090	2490	1/4	5.0
C1b[a]	1570	3660	1/4	5.0

[a] These atoms have population factors set to 0.5.

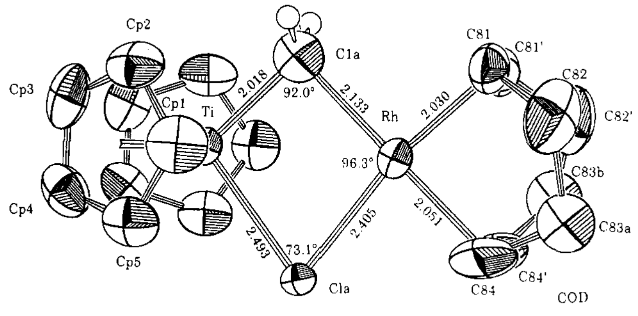

Figure 2. ORTEP of $Cp_2TiRh(COD)(\mu\text{-}CH_2)(\mu\text{-}Cl)$ view normal to metallacycle (Cla–Ti–Cl angle = 96.7°).

In order to address this and other structural issues, a crystal of **3a** suitable for X-ray structure determination was obtained by slow of cooling a toluene/pentane solution. Details of the data collection are summarized in Table II. Fractional coordinates of non-hydrogen atoms are given in Table III; bond lengths and bond angles are presented in Table IV. The structure of **3a** (Figure 2) consists of a four-membered ring lying in a mirror plane with a cyclopentadienyl ring above and below this plane and the double bonds of the COD ligand perpendicular to and

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[9] Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

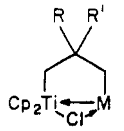
Table IV. Bond Lengths (Å) and Bond Angles (deg)[a]

atom	atom	distance	atom	atom	distance
Rh	Ti	2.986 (2)			
Rh	Cla	2.405 (4)	Rh	Clb	2.432 (5)
Rh	C1a	2.133	Rh	C1b	2.073
Ti	Cla	2.493 (5)	Ti	Clb	2.462 (5)
Ti	C1a	2.018	Ti	C1b	2.011
Ti	Cp0	2.071			
Cp1	Cp2	1.374 (11)	Cp1	Cp5	1.401 (11)
Cp2	Cp3	1.389 (11)	Cp3	Cp4	1.378 (11)
Cp4	Cp5	1.393 (11)	C81	C82	1.494 (11)
C81	C81′	1.332 (9)	C82	C83a	1.342 (22)
C82	C83b	1.581 (20)	C83a	C84	1.644 (22)
C83b	C84	1.423 (20)	C84	C84′	1.416 (13)

atom	atom	atom	angle	atom	atom	atom	angle
Cla	Rh	C1a	96.3 (1)	Clb	Rh	C1b	95.1 (1)
Cla	Ti	C1a	96.7	Clb	Ti	C1b	95.8
Cla	Ti	Cp0	104.7	Clb	Ti	Cp0	104.9
C1a	Ti	Cp0	106.9	C1b	Ti	Cp0	107.0
Ti	Cla	Rh	75.1 (1)	Ti	Clb	Rh	75.2 (2)
Ti	C1a	Rh	92.0	Ti	C1b	Rh	94.0
Cp5	Cp1	Cp2	108.6 (7)	Cp3	Cp2	Cp1	106.4 (7)
Cp4	Cp3	Cp2	110.6 (7)	Cp5	Cp4	Cp3	106.2 (7)
Cp4	Cp5	Cp1	108.2 (7)	C81′	C81	C82	124.6 (7)
C83a	C82	C81	116.9 (11)	C83b	C82	C81	112.4 (9)
C84	C83a	C82	111.5 (14)	C84	C83b	C82	110.8 (12)
C84′	C84	C83a	136.3 (10)	C84′	C84	C83b	106.5 (10)

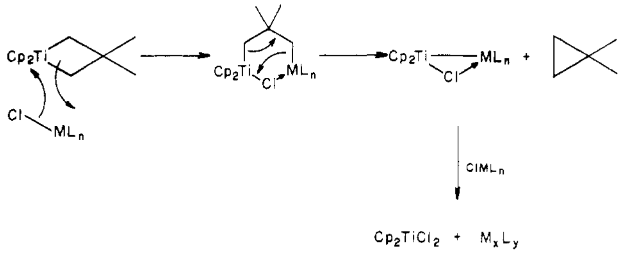
[a] C81′ and C84′ are generated from C81 and C84 by the mirror plane. Cp0 is the center of mass of the unique cyclopentadiene ring.

nearly bisected by it. The Ti-Rh bond length of 2.98 Å is sufficiently short that some direct metal-metal interaction is possible. For example the Ti-Rh distance is 2.68 Å[10] in an alloy of the two metals, and the Ti-Rh distance in a highly reduced Rh and titania is 2.55 Å.[11] It is also 0.15 Å longer than the Ti-Rh distance in the corresponding μ-CH$_2$, μ-CH$_3$ analogue.[4] We note that the overall structure is consistent with a pseudotetrahedral Ti(IV) and square-planar Rh(I) bonding description. If this description is accurate, then a filled Rh $d_{xy}(b_{2g})$ orbital is directed at an empty $2a_1$ orbital on Ti. Such a dative Rh→Ti interaction, if important, should reduce the electron density on Rh. Such an effect will be examined in future reactivity studies.



Because the metallacyclic ring of **3a** was disordered due to random transposition of the μ-CH$_2$ and μ-Cl groups in the crystals, it was not possible to obtain accurate information on the μ-CH$_2$ bonding. It is interesting to note that the Rh-CH$_2$ bond length (average) of 2.10 Å is equivalent to that found in the methyl-bridged analogue.[4] The Ti-Cl bond length of 2.48 Å is among the longer terminal Ti-Cl bonds (ca. 2.24-2.46 Å)[12,13] but shorter than most other reported Ti-Cl bridged bonds (ca. 2.57-2.59 Å).[13] The Rh-Cl bonds average 2.42 Å, only slightly longer than the value of 2.38 Å seen in the [(COD)RhCl]$_2$.[14] The Ti–C–Rh angle of 93° is significantly greater (9°) than the analogous angle in the methyl-bridged compound.[4]

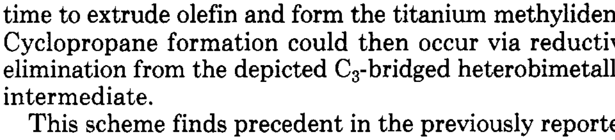
Scheme I. The Proposed Mechanism for Cyclopropane Formation



The calculated bond length for a Ti=CH$_2$ double bond is 1.85–1.88 Å,[15] and the Ti-C distance in Cp$_2$Ti–CH$_2$–CH(C(CH$_3$)$_3$)–CH$_2$ is 2.15 Å.[2,16] The observed bond length of 2.02 Å suggests again some residual multiple bonding between the Ti and CH$_2$ in the complex.

The unique cyclopentadienyl group is normal, with an average C–C bond length of 1.38 Å and an average bond angle of 108.0°. The bond lengths and angles in the COD ligand show many anomalous values due to disorder (see Experimental Section).

Ancillary Ligand Effect. The outcome of the reactions of $(\eta^5\text{-}C_5H_5)_2TiCH_2CRR'CH_2$ titanacyclobutanes with XML$_n$ complexes (X = halide; M = late transition metal; L$_n$ = ancillary ligands) depends markedly upon the nature of the ancillary ligands. Whereas the reaction of the titanacyclobutane **1a** with [(Cl)Rh(1,5-COD)]$_2$ gives a quantitative crude yield of the μ-CH$_2$ compound **3a**, the corresponding reaction with [(Cl)Rh(CO)$_2$]$_2$ produces no μ-CH$_2$ product, giving instead dimethylcyclopropane. If an excess of the metal halide is employed, quantitative yields of the cyclopropane product are observed, along with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and an intractable black precipitate, presumed to contain Rh$_x$(CO)$_y$ species (eq 2). Similar results are observed with Cl$_2$Pd(PhCN)$_2$. These reactions are rapid at 25 °C, and no intermediates have been detected, either at 25 °C or at low temperatures.



(2)

A common feature of the metal halides involved in these cyclopropane-forming reactions is that they all contain highly electrophilic metal centers. This confers sufficient reactivity upon these centers to attack the Ti–C bond of the titanacyclobutane (Scheme I) before the latter has had time to extrude olefin and form the titanium methylidene. Cyclopropane formation could then occur via reductive elimination from the depicted C$_3$-bridged heterobimetallic intermediate.

This scheme finds precedent in the previously reported reaction of titanacyclobutanes with I$_2$ to form cyclopropanes and $(\eta^5\text{-}C_5H_5)_2TiI_2$[18] and the reaction of titanacyclobutanes with alkyl aluminum halides. A γ-iodopropyltitanium intermediate analogous to the proposed C$_3$-bridged heterobimetallic species shown in Scheme I was detected in the I$_2$ reaction. Also relevant are the reports of cyclopropane formation by reductive elimination from dimetallacyclopentane complexes.[17]

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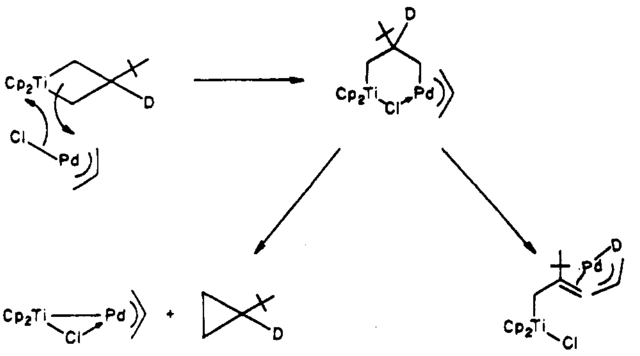
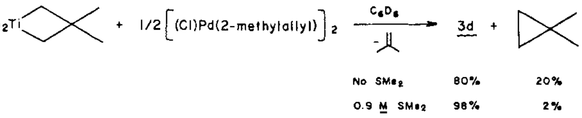
Scheme II. The Proposed Mechanism for the Reaction of 1c with $[(Cl)Pd(\pi\text{-allyl})]_2$



Although the μ-CH_2 compound is the major product (80%) of the reaction of $[(Cl)Pd(2\text{-methylallyl})]_2$ with titanacyclobutane **1a**, dimethylcyclopropane is produced as a side product in 20% yield. Studies of the reaction of $[(Cl)Pd(\eta^3\text{-allyl})]_2$ with the titanacyclobutane **1c** (eq 3)

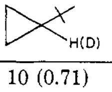
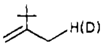
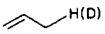


(3)

proved most informative. As indicated by Scheme II, the reaction with this titanacyclobutane differs from the corresponding reaction of titanacyclobutane **1a** in that (i) no μ-CH_2 product is formed and (ii) propene and 2-*tert*-butylpropene are observed as coproducts. The absence of any μ-CH_2 product is attributed to the greater thermal stability of **1c** relative to **1a**. Whereas **1a** serves as a titanium methylidene source at 25 °C, **1c** is stable at 25 °C and must be heated to 65 °C to achieve a convenient rate of reaction.[19] The reaction of **1c** with $[(Cl)Pd(\pi\text{-allyl})]_2$ at 25 °C evidently therefore proceeds exclusively via attack by the Pd complex upon the intact titanacyclobutane. As shown in Scheme II, all three hydrocarbon products are proposed to arise from the C_3-bridged heterobimetallic intermediate in Scheme I. A β-H elimination reaction of this intermediate is proposed to give rise to the olefinic products. The fact that olefins are not observed in the corresponding reaction of **1a** is thus attributable to the fact that **1a** has no β-H. In the reaction of **1c** with $Cl_2Pd(PhCN)_2$ or $[(Cl)Rh(CO)_2]_2$, both *tert*-butylcyclopropane and *tert*-butylpropene are again observed. A mechanism similar to that of Scheme II is proposed. Analogous mechanisms have been proposed to explain the formation of cyclopropane and propene in the decomposition of 1,2-dimetallacyclopentanes.[18]

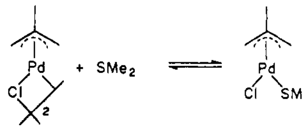
A key feature of the mechanism given in Scheme II is that the *tert*-butylcyclopropane and olefinic products are formed from a common intermediate in a partition that should reflect the relative rates of *tert*-butylcyclopropane formation and β-H elimination. Substitution of a β-D for the β-H in this intermediate would be expected to affect this partition, so the reaction of **1c**-β-*d* with $[(\eta^3\text{-allyl})(\mu\text{-}Cl)Pd]_2$ was examined as a test of the proposed mechanism. The *tert*-butylcyclopropane, 2-*tert*-butylpropene, and propene produced were analyzed by ^1H and ^2H NMR, capillary GC, and GC/MS methods. The combined yield of these products was >95% based on **1c** by NMR integration against an internal standard. ^2H NMR analysis showed deuterium to be incorporated only at the *tert*-butylcyclopropane 1-position, the 2-*tert*-butylpropene 3-position, and the propene 3-position. However, while the *tert*-butylcyclopropane and 2-*tert*-butylpropene retained all or most of the D label, the propene generated upon reaction in C_6D_6 was roughly 50% nondeuteriated. It is evident from this result that the mechanism is likely to be more complicated than that given in Scheme II and may involve H-atom abstraction (from the solvent or other sources). It is still important to note, however, that a substantial isotope effect upon the product distribution is observed. As shown in Table V, reaction of the β-D titanacyclobutane produces significantly more *tert*-butylcyclopropane and less of the two olefins. While the ratio of the two olefins is almost unchanged within experimental error, the relative amount of *tert*-butylcyclopropane to *total olefin* is a factor of 2–4 times greater with the β-D reagent. These results suggest that the mechanism of Scheme II is substantially correct, especially with regard to the proposed involvement of the C_3-bridged heterobimetallic intermediate. The formation of propene-d_0 from **1c**-β-*d* may simply reflect the involvement of an H-atom abstraction step subsequent to the product partitioning steps.

Table V. The Hydrocarbon Product Yields and Ratios Observed for the Reaction of $[(\eta^3\text{-allyl})(\mu\text{-}Cl)Pd]_2$ with 1c and 1c–β-*d*

	yields^a (ratios)		
reagents	 H(D)	 H(D)	 H(D)
1c	10 (0.71)	14 (1)	76 (5.4)
1c-β-*d*	26 (2.4)	11 (1)	63 (5.7)

^{a} Percent based on **1c**.

As noted previously, dimethylcyclopropane is an undesired side product of the reaction of **1a** with **2d** to form the μ-CH_2 compound **3d**. The above experiments suggested that the formation of this side product occurred because the Pd reagent was excessively electrophilic. A masked form of the Pd reagent was accordingly sought. This was achieved through the addition of the weak ligand SMe_2. ^1H NMR experiments showed that the equilibrium represented by eq 4 is rapid on the NMR time scale and



(4)

at the concentrations employed it is driven almost entirely to the right through the addition of 2 equiv of SMe_2/equiv of Pd. The effect of added SMe_2 upon the course of the titanacyclobutane reaction is shown below. In the absence of SMe_2 a 20% yield of dimethylcyclopropane is observed, while the addition of SMe_2 reduces that yield to 2%. A similar effect is observed upon addition pyridine. Neither ligand forms stable complexes with the μ-CH_2 product, although both accelerate the rate of π–σ–π isomerization in the Pd complex.

While the above presented modification constitutes a high yield approach to **3d**, it suffers from the fact that **3d** is thermally unstable at the reaction temperature (25 °C) and a small amount of decomposition is unavoidable. In seeking a low-temperature route to **3d**, it was discovered that Tebbe's reagent $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$[20]

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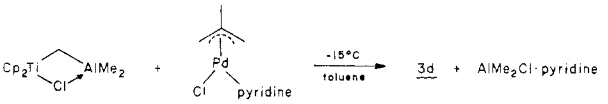
[17] (a) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694. (b) Cooke, M.; Forrow, N. J.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2435.

[18] Ho, S. C. H.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 1533.

[19] Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406.

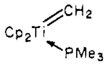
reacts with the pyridine complex of the Pd reagent at −15 °C (eq 5) to give a 70% yield of crystalline **3d**. The only



(5)

significant side product is the corresponding μ-CH_2, μ-CH_3 compound **3i** resulting from the reaction of **3d** with methylaluminum compounds. Since the titanacyclobutane **1a** is prepared from Tebbe's reagent,[16] the preparation of **3d** directly from the latter results in a shorter synthesis with a higher overall yield.

Another source of the titanium methylidene fragment that was also examined was the PMe_3 adduct **4**.[21] The reaction of this complex with $((\eta^3\text{-allyl})(\mu\text{-Cl})Pd)_2$ gave a μ-CH_2 compound identified by ^1H NMR to be the σ-allyl analogue of **3d** $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-Cl})Pd(\eta^1\text{-allyl})PMe_3$. However, the Pd-bound PMe_3 ligand is evidently labile since attempted crystallization gave only the corresponding phosphine-free η^3-allyl complex. The PMe_3 ligand bound to the titanium methylidene starting material is also labile and can induce to side reactions by coordinating to the metal halide starting material. For example, in the reaction of 4 with $Rh(CO)(Cl)(SMe_2)_2$, a mixture of $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-Cl})Rh(CO)PMe_3$, the corresponding SMe_2 complex **3g**, and an unidentified $Rh(PMe_3)$ complex are observed. The PMe_3 adduct 4 therefore appears less suitable than the titanacyclobutanes or Tebbe's complexes for the preparation of μ-CH_2 complexes.



4

Conclusions

The reaction of sources of $Cp_2Ti{=}CH_2$ with late-transition-metal halides with a labile ligand is a direct route to a family of early–late-transition-metal μ-methylene complexes. This series provides excellent entries into studies of the structure and reactivity of this important class of compounds.

Experimental Section

General Considerations. All manipulations were carried out under argon with standard Schlenk techniques or in a nitrogen-filled glovebox equipped with a −40 °C freezer. Argon was purified by passage through columns of Chemalog R3-11 catalyst and Linde 4-Å molecular sieves. Toluene, benzene, diethyl ether, pentane, THF, and hexane, including NMR solvents, were stirred over CaH_2 and transferred onto sodium benzophenone ketyl. Solvents dried in this manner were vacuum transferred and stored under argon in flasks equipped with Teflon screw valves.

^1H NMR spectra were recorded in C_6D_6, $CDCl_3$, or C_7D_8 by using residual protio solvent resonances as an internal reference on Varian EM-390, JEOL FX90Q, JEOL GX400, or Bruker WM-500 spectrometers. ^{13}C spectra were obtained on the JEOL instruments. IR spectra were recorded as Nujol mulls or in solution in C_6D_6 on Beckman IR-4200 or Shimadzu IR-435 instrument. Elemental analyses were performed at the California Institute of Technology Analytical Facility or by Dornis and Kolbe Microanalytical Laboratory. All reactions were carried out at room temperature unless otherwise indicated.

Preparation of Starting Materials. The following compounds were prepared according to literature procedures or purchased commercially: $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-Cl})AlMe_2$,[20] **1a**,[2] **1b**,[2] **1c**,[19] **2a**,[22] **2b**,[23] **2c**,[24] **2d**,[25] **2e**,[9] **2f**,[26] **2g**,[18] $[(Cl)Rh(CO)_2]_2$, $PdCl_2(PhCN)_2$, $[(Cl)Pd(\eta^3\text{-allyl})]_2$. Compound **1c-$\beta$-*d*** was prepared from **1a** and 3,3-dimethyl-2-deuteriobutene according to the procedure used to prepare **1c**. Compound **2h** was prepared from $[Rh(C_2H_4)_2(\mu\text{-Cl})]_2$[26] and SMe_2 following a procedure analogous to that used to prepare **2g**.

Preparation of the μ-CH_2 Complexes. Preparation of 3a. Solid **1b** (0.25 g, 0.90 mmol) and **2a** (0.22 g, 0.89 mmol) were combined in a 15-mL Schlenk tube equipped with a magnetic stirring bar. Toluene (2 mL) was added with stirring to produce a red solution from which the product immediately began to precipitate as a red powder. After being stirred for 2 h at 25 °C, the mixture was diluted with pentane (4 mL) and let stand 3 h at 25 °C, 24 h at 0 °C, and 48 h at −20 °C. The mixture was then chilled to −70 °C, and the supernatant was removed via cannulation through a filter paper tipped cannula. The solid was washed with cold pentane (15 mL). The resultant crude product was redissolved in toluene (10 mL), filtered, diluted with pentane, and filtered again. The product crystallized upon standing (18 h at 25 °C, 25 h at 0 °C, 48 h at −20 °C). The supernatant was removed via cannula, and the crystalline residue was dried in vacuo to give 0.28 g (70%) of red crystals, suitable for X-ray diffraction: ^1H NMR (C_6D_6) δ 7.48 (2, s, μ-CH_2), 5.50 (10, s, Cp), 4.97 (2, m, COD olefinic), 3.95 (2, m, COD olefinic), 1.3–2.4 (8, br m, COD methylene); ^{13}C NMR (C_6D_6) δ 186.5 (t of d, J = 128 Hz, 20 Hz, μ-CH_2), 107.9 (d of m, J = 173 Hz, Cp), 89.5 (d of m, J = 155 Hz, COD olefinic), 77.1 (d of d, J = 155 Hz, 16 Hz, COD olefinic), 33.0 (t, J = 128 Hz, COD methylene), 29.9 (t, J = 128 Hz, COD methylene). Anal. Calcd for $C_{19}H_{24}ClRhTi$: C, 52.02; H, 5.51; Cl, 8.08. Found: C, 52.05; H, 5.48; Cl, 8.06.

X-ray Structure Determination. A crystal of $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-Cl})Rh$(1,5-cyclooctadiene) was mounted in a glass capillary tube under a nitrogen atmosphere. Preliminary photographs indicated monoclinic or higher symmetry. Intensity data were collected by using an Enraf-Nonius CAD4 diffractometer with a graphite monochromator and Mo Kα radiation. Systematic absences ($0k\ell$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$) indicated either the centrosymmetric space group *Pbcm* or the noncentrosymmetric space group $Pbc2_1$. Counting statistics favored the centrosymmetric space group. The unit-cell parameters (orthorhombic) were obtained by least-squares refinement of the θ values of 20 reflections in the range: $9.8 < \theta < 15.9°$. A total of 6814 intensity measurements were recorded for reflections in one hemisphere ($2\theta \leq 50°$) by using θ–2θ scans at a variable scan speed (1.44–4.02°/min). Three check reflections were remeasured after every 5.5 h of exposure time and indicated a slight decay (ca. 3.5%) over the 108 h of data collection. Absorption corrections were not applied. After averaging over the Laue symmetry and reducing to F_o^2, the total number of unique data were 1568 of which 1061 had $F_o > 3\sigma(F_o)$.

The position of the Rh atom was derived from a Patterson map, and subsequent Fourier and difference maps revealed all non-hydrogen atoms. Atomic scattering factors were taken from Stewart, Davidson, and Simpson[27] for H and ref 28 for all others. The anomalous dispersion corrections for Ti, Rh, and Cl were included. The peaks for the carbon and chlorine atoms of the metallacycle were approximately equal in size in a Fourier map. This indicated that the structure was actually a statistical mixture of two possible orientations. The bridging chlorine atom was put in two possible orientations with population one-half, and a subsequent difference map showed the locations of the half-population carbon atoms, approximately 0.4 Å from the chlorine atoms. Refinement was carried out keeping the positions of these carbon atoms fixed while varying the chlorine atom positions (one

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(26) Purchased from Strem Chemicals Co.

(27) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(28) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, 1974; Vol. IV, pp 72–97.

attempt to refine both chlorine and carbon atoms led to unreasonable results). After the refinement, a difference Fourier map was used to correct the carbon atom positions. This process was repeated several times until no further change in the carbon atom positions was necessary.

The thermal ellipsoids for one of the cyclooctadiene carbon atoms indicated possible disorder. Also the bond lengths to this atom were abnormally short. A close examination of a difference map indicated that this atom (C83) was disordered and, further, that the two carbons attached to it (C82 and C84) were also probably disordered. However, attempts to model the disorder of C82 and C84 were unsuccessful. The best model obtained has disorder only in C83. Least-squares refinement of all non-hydrogen parameters with anisotropic U's (except the disorder COD atom with an isotropic U), minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$ on all parameters yielded $R = 0.069$, $R_{3\sigma} = 0.048$, and $S = 3.09$,[29] final shift/errors < 0.10. Hydrogen atoms were placed at a distance of 0.95 Å by assuming ideal geometry with isotropic U's = 0.063 Å^2 and were not refined. The disorder in the bridging methylene group and the cyclooctadiene group precluded the location of the hydrogen atoms on these groups. The calculated positions of the hydrogen atoms of the cyclopentadienyl group were verified on a difference Fourier map.

All calculations were carried out on a VAX 11/780 or VAX 11/750 computer using the CRYRM system of programs.

Preparation of 3b. A procedure similar to that given above was followed to obtain **3b**, which crystallizes with difficulty from toluene/pentane (1:6) at −50 °C: ^{1}H NMR (C_6D_6) δ 7.21 (2, s, μ-CH_2), 5.50 (10, s, Cp), 4.25 (2, m, COD olefinic), 3.78 (2, m, COD olefinic), 3.22 (s, OMe), 1.4–1.5 (8, m, COD methylene). Anal. Calcd for $C_{20}H_{27}ORhTi$: C, 55.32; H, 6.27. Found: C, 54.98; H, 6.34.

Preparation of 3c. A procedure similar to that used to prepare **3a** was followed to obtain **3c** as dark red crystals from toluene/ether (1:1) at −50 °C in 82% yield: ^{1}H NMR (C_6D_6) δ 7.95 (2, s, μ-CH_2), 5.42 (10, s, Cp), 4.57 (2, m, COD olefinic), 3.71 (2, s, COD olefinic), 1.3–2.4 (8, m, COD methylene); ^{13}C NMR (C_6D_6) δ 180.7 (t, J = 132 Hz, μ-CH_2), 107.2 (d of m, J = 174 Hz, Cp), 70.4 (d, J = 153 Hz, COD olefinic), 62.1 (d, J = 156 Hz, COD olefinic), 33.0 (t, J = 134 (±6) Hz, COD methylene), 30.4 (t, J = 134 (±6) Hz, COD methylene). Anal. Calcd for $C_{19}H_{24}ClIrTi$: C, 43.23; H, 4.58; Cl, 6.72. Found: C, 43.30; H, 4.57; Cl, 6.58.

Preparation of 3d. (a) From Tebbe's Reagent. (η^5-$C_5H_5)_2Ti(\mu$-$CH_2)(\mu$-$Cl)AlMe_2$ (1.0 g, 3.5 mmol) and chloro(η^3-2-methylallyl)(pyridine)palladium (0.97 g, 3.5 mmol) were combined in a 100-mL Schlenk flask equipped with a stirring bar. The flask was immersed in a −35 °C cold bath, and toluene (10 mL) was added to give a dark red solution. The temperature was allowed to rise over a 15-min period to −15 °C and then maintained at −15 ± 2 °C for 20 min. The solution was then diluted (at −15 °C) with ether (10 mL) and then pentane (15 mL). This mixture was slowly cooled to −50 °C and let stand for 48 h to effect crystallization. After this time, the supernatant was removed through a filter paper tipped cannula and the solid was washed with pentane at −50 °C and then dried in vacuo. This gave 0.96 g (70%) yield of small black crystals. The compound is thermally sensitive, and decomposes at 25 °C in solution ($\tau_{1/2}$ of ca. 20 h starting with pure **3d**) and even in the solid state (the decomposition being perceptible after several weeks at 25 °C). It is indefinitely stable in the solid state at −20 °C: ^{1}H NMR (C_6D_6, designations as per Figure 1) δ 8.17 (1, d, J = 7.3 Hz, H_{b_1}), 7.90 (1, d, J = 7.3 Hz, H_{b_2}), 5.55 (5, s, Cp^1), 5.48 (5, s, Cp^2), 4.12 (1, d, J = 2.9 Hz, H_{s_2}), 3.09 (1, d of d, J = 2.9 Hz, 1.5 Hz, H_{s_1}), 2.87 (1, s, H_{a_2}), 2.58 (1, d, J = 1.5 Hz, H_{a_1}), 1.46 (3, s, Me). ^{1}H NMR decoupling: irradiation of H_{a_1} resonance at δ 2.58 causes H_{s_1} resonance at δ 3.09 to collapse to a doublet, J = 2.9 Hz; irradiation of H_{s_1} resonance at δ 3.09 causes H_{s_2} resonance at δ 4.12 and H_{a_1} resonance at δ 2.58 to collapse to singlets. ^{1}H NOE (enhanced peaks listed in decreasing order of enhancement): irradiation of H_{s1} resonance enhanced those due to H_{a_1}, Me, H_{b_2}, H_{b_1}; irradiation of H_{b_2} resonance enhanced those due to H_{b_1}, Cp_2, H_{s_1}; irradiation of H_{a_1} resonance enhanced those due to H_{s_1}, H_{a_2}, H_{b_1}; irradiation of H_{b_1} resonance enhanced those due to H_{b_2}, Cp_1, H_{a_1}, H_{s_1}; irradiation of H_{s2} resonance enhanced those due to H_{a_2}, Me. Anal. Calcd for $C_{15}H_{19}ClPdTi$: C, 46.31; H, 4.92. Found: C, 46.39; H, 4.84.

(b) From Titanacyclobutane 1a (^{1}H NMR Experiment). A solution of**2d** (0.010 g, 0.051 mmol) in 0.25 mL of C_6D_6 was added to a solution of **1a** (0.012 g, 0.048 mmol) in 0.25 mL of C_6D_6 to give a dark red solution and a flocculent black precipitate of Pd metal. ^{1}H NMR analysis showed this solution to contain a mixture of **3d** (80% yield based on the liberated isobutene coproduct) and dimethylcyclopropane (20%), characterized as such on the basis of comparison with its reported spectrum and by analogy with the more fully characterized *tert*-butylcyclopropane producing reaction of **1c** with $[(Cl)Pd(\eta^3$-allyl)$]_2$, discussed below.

(c) From Titanacyclobutane 1a and 2d in the Presence of SMe_2 (^{1}H NMR Experiment). A solution of **2d** (0.020 g, 0.10 mmol) in 0.25 mL of C_6D_6 containing SMe_2 (15 μL, 0.20 mmol) was added to a solution of **1a** (0.025 g, 0.10 mmol) in a 0.25 mL of C_6D_6 to give a dark red solution. ^{1}H NMR analysis showed this solution to contain **3d** (98% based on the liberated isobutene coproduct) and a trace (2%) of dimethylcyclopropane. ^{1}H NMR with added SMe_2 (0.4 M) (shown in Figure 1): δ 8.02 (2, center of nearly collapsed μ-CH_2 AB quartet), 5.51 (10, s, Cp), 4.11 (1, br s, H_{s_2}), 3.05 (1, v br s, H_{s_1}), 2.87 (1, s, H_{a_2}), 2.62 (1, v br s, H_{a_1}), 1.72 (12, s, SMe_2), 1.46 (3, s, Me).

Preparation of 3e. Compounds **1a** (0.124 g, 0.500 mmol) and **2e** (0.185 g, 0.500 mmol) were combined and dissolved in 1 mL of toluene to obtain a clear red solution. Removal of the volatiles under reduced pressure gave **3e** as a red oil, pure by NMR: ^{1}H NMR (C_6D_6) δ 7.42 (2, s, ^2J(PtH) = 46.9 Hz, μ-CH_2), 5.57 (10, s, Cp), 1.96 (6, s, ^3J(PtH) = 31.7 Hz, SMe_2), 1.09 (3, s, ^2J(PtH) = 93.3 Hz, PtMe). ^{1}H NOE (C_6D_6): irradiation of the μ-CH_2 resonance enhanced the cyclopentadienyl and Pt–Me resonances; irradiation of the Pt–Me resonance enhanced the μ-CH_2 resonance. Irradiation of the SMe_2 resonance did not affect any of the other resonances and vice versa. ^{13}C NMR (C_6D_6): δ 152.7 (t, J(CH) = 136 Hz, J(PtC) = 580 Hz, μ-CH_2), 108.7 (d of m, J(CH) = 173 Hz, Cp), 22.7 (qrt, J(CH) = 140 Hz, ^2J(PtC) = 10 Hz, SMe_2), −12.0 (qrt, J(CH) = 130 Hz, J(PtC) = 855 Hz, PtMe).

Preparation of 3f–h. Compounds **3f–h** were prepared from **1a** and **2f–h**, respectively, by dissolution of equimolar mixtures of the solid reagents in C_6D_6. The products were characterized without isolation by NMR spectroscopy. Compound **3f** was pure by NMR but decomposed slowly at 25 °C over a period of 1 week, with deposition of a gold mirror. Compound **3g** was formed in high yield but decomposed within 1 h at 25 °C. Compound **3h** was similarly formed in high yield but decomposed upon removal of the volatiles under reduced pressure. **3f**: ^{1}H NMR (C_6D_6) δ 6.91 (2, d, ^3J(PH) = 5.4 Hz, μ-CH_2), 5.95 (10, s, Cp), 0.88 (9, d, ^2J(PH) = 9.2 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 1.82 (s, PMe_3). **3g**: ^{1}H NMR (C_6D_6) δ 7.48 (2, s, μ-CH_2), 5.48 (10, s, Cp), 1.94 (6, s, SMe_2); ^{1}H NMR (C_6D_6) δ 6.77 (2, s, μ-CH_2), 5.51 (10, s, Cp), 3.16 (4, br s, C_2H_4), 1.75 (br s, assigned to coordinated SMe_2 in exchange with excess free SMe_2).

Reaction of 1c with $[(\eta^3$-allyl)$(\mu$-Cl)Pd$]_2$. Compound **1c** (0.028 g, 0.10 mmol) and $[(\eta^3$-allyl)$(\mu$-Cl)Pd$]_2$ (0.041 g, 0.22 mmol) were combined in a 10-mL flask equipped with a stirring bar. Toluene-d_8 (0.40 mL) was added, the flask was fitted with a closed valve (to prevent loss of propene), and the mixture was stirred. A dark red solution and copious amounts of a flocculant black precipitate of Pd metal were obtained. The volatiles were vacuum transferred into a 5-mm NMR tube. The tube was then sealed, and the 400-MHz ^{1}H NMR spectrum was recorded. Comparison with authentic samples showed this sample to contain propene (75%), 2-*tert*-butylpropene (15%) and *tert*-butylcyclopropane (10%). Yields were determined by integration against an internal standard and are based on **1c**. Quantitative capillary GC analysis using authentic samples for comparison similarly showed the sample to contain propene (76%), 2-*tert*-butylpropene (13%), and *tert*-butylcyclopropane (11%).

Reaction of 1c-β-*d* with $[(\eta^3$-allyl)$(\mu$-Cl)Pd$]_2$. The above procedure was repeated using **1c**-β-*d*. The 400-MHz ^{1}H NMR analysis yielded the following ratios: propene (59%), 2-*tert*-butylpropene (13%), *tert*-butylcyclopropane (28%). Capillary GC analysis gave similar ratios: propene (66%), 2-*tert*-butylpropene (10%), *tert*-butylcyclopropane (24%). ^{2}H NMR analysis showed deuterium to be incorporated only at the propene 3-position, the

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(29) $R = \sum|F_o - |F_c||/\sum|F_o|$; $S = \sqrt{\sum w\Delta/(n-p)}$; $R_{3\sigma} = R$ for reflections with $F_o > 3\sigma(F_o)$; $\Delta = F_o^2 - F_c^2$.

2-*tert*-butylpropene 3-position, and the *tert*-butylcyclopropane 1-position. Integration of the ^{2}H NMR peaks against an internal standard (C_6D_6 or C_7D_8) allowed rough estimates of the levels of deuterium incorporation and showed the 2-*tert*-butylproene and *tert*-butylcyclopropane to contain, on average, one deuterium/molecule and the propene to contain 0.5 deuterium/molecules.

Reaction of 1a or 1c with $[Rh(CO)_2(\mu\text{-}Cl)]_2$ or $PdCl_2(PhCN)_2$. The reaction of **1c** with excess $[Rh(CO)_2(\mu\text{-}Cl)]_2$ or $PdCl_2(PhCN)_2$ according to the procedure given above for the corresponding $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ reaction gave a mixture of *tert*-butylcyclopropane, 2-*tert*-butylpropene, $(\eta^5\text{-}C_5H_5)_2TiCl_2$, and an intractable black precipitate of (presumably) $Rh_x(CO)_y$ or Pd metal. The ratio of *tert*-butylcyclopropane to 2-*tert*-butylpropene was roughly 82:18 for both reactions. The corresponding reactions of **1a** gave dimethylcyclopropane.

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Registry No. **1a**, 80122-07-2; **1b**, 90076-32-7; **1c**, 75687-68-2; **1c**-β, 117119-24-1; **2a**, 12092-47-6; **2b**, 12148-72-0; **2c**, 12112-67-3; **2d**, 12081-18-4; **2e**, 87145-39-9; **2f**, 15278-97-4; **2g**, 56954-39-3; **2h**, 117119-25-2; **3a**, 90076-34-9; **3b**, 90076-35-0; **3c**, 90076-36-1; **3d**, 117119-19-4; **3e**, 117119-20-7; **3f**, 117119-21-8; **3g**, 117119-22-9; **3h**, 117119-23-0; $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$, 67719-69-1; $[(\eta^3\text{-allyl})(\mu\text{-}Cl)Pd]_2$, 12012-95-2; $[Rh(CO)_2(\mu\text{-}Cl)]_2$, 14523-22-9; $PdCl_2(PhCN)$, 14220-64-5; chloro(η^3-2-methylallyl)(pyridine)palladium(II), 50497-55-7; dimethylcyclopropane, 1630-94-0; propene, 115-07-1; 2-*tert*-butylpropene, 594-56-9; *tert*-butylcyclopropane, 4741-87-1; propene-3d_1, 1117-89-1; 2-tert-butylpropene-*3*-d_1, 117021-99-5; *tert*-butylcyclopropane-*1*-d_1, 117022-00-1; $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$, 12122-73-5.

Supplementary Material Available: Tables of Gaussian amplitudes and hydrogen atom coordination (1 page); a listing structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Equilibrium Studies of Thiophene Exchange in (η-Thiophene)Ru(η-C_5H_5)$^+$: A Model for Thiophene Adsorption on Hydrodesulfurization Catalysts

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Equilibrium constants (K') for the displacement of the π- (i.e., η^5-) thiophene (T) ligand in CpRu(T)$^+$ by methyl-substituted thiophenes (Th′), $CpRu(T)^+ + Th' \rightleftharpoons CpRu(Th')^+ + T$, increase as the number of methyl groups in Th′ increases: T (1) < 2-MeT (6) < 3-MeT (7) < 2,5-Me_2T (35) < 2,3-Me_2T (50) < 2,3,4-Me_3T (200) < 2,3,5-Me_3T (300) < Me_4T (1300). The K' values increase by a factor of approximately 6 for each methyl in the thiophene (Th′). That thiophenes also adsorb to a Co–Mo/Al_2O_3 HDS catalyst more strongly as the number of methyl groups in the thiophene increases suggests that they are also π-bonded to the catalyst surface. The results suggest that trends in rates of deuterium exchange and hydrodesulfurization on HDS catalysts for a series of methyl-substituted thiophenes are determined by their relative strengths of adsorption to the catalyst surface.

Introduction

Catalytic hydrodesulfurization (HDS), the process by which sulfur is removed from crude oil by treatment with hydrogen over a Mo–Co/γ-Al_2O_3 catalyst, is practiced industrially on a very large scale.[2] Despite a large number of studies, little is understood about the basic steps of this process,[3] especially for thiophene compounds which are the most difficult to desulfurize. The first question concerns the binding mode of the thiophene to the catalyst. Three types of adsorption have been proposed: via the S-atom only,[4] as a π-complex involving the unsaturated carbon atoms,[5] or via the entire π-system in an η^5-fashion.[6,7]

One approach to understanding the HDS activity of thiophenes is to prepare thiophene transition-metal complexes and to compare their reactivities with that of thiophene on HDS catalysts. Only a few S-coordinated thiophene complexes (where T = thiophene) are known: $Ru(NH_3)_5(T)^{2+}$,[8] $CpFe(CO)_2(T)^+$,[9] $W(CO)_3(PCy_3)_2(T)$,[10] and $Ru(PPh_3)_2(CpCH_2C_4H_3S)^+$, in which the thiophene is attached to the cyclopentadienyl ligand.[11] No reactions of these rather unstable S-coordinated complexes have been reported. More common are compounds with η^5-thiophene coordination: $(CO)_3Cr(T)$,[12] $(CO)_3Mn(T)^+$,[13] $CpM(T)^+$ (M = Fe,[14] Ru[15–17]), $Cp^*M(T)^{2+}$ (M = Rh, Ir),[18] $(PPh_3)_2M(T)^+$ (M = Rh, Ir).[19] The Ru complex is noteworthy because on the one hand, Ru is an excellent HDS

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