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Synthesis and Reactivity of Permethyltantalocene Derivatives Possessing η^3-Allyl, η^2-Butadiene, η^2-Methylallene, and η^1-Alkenylidene Ligands. Model Studies for the Role of Surface Vinylidenes in the Fischer–Tropsch Hydrocarbon-Chain-Lengthening Process[†]

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The reactivity of $Cp^*_2TaH_3$ (**2**) ($Cp^* = \eta^5\text{-}C_5Me_5$) toward a number of conjugated dienes has been investigated, and mechanistic pathways have been probed by deuterium-labeling studies. Treatment of **2** with allene at 50 °C affords $Cp^*_2Ta(\eta^3\text{-}C_3H_5)$ (**3**), which, according to ^1H and ^{13}C NMR data, is most reasonably described as a tantalabicyclobutane complex. Warming at 80 °C converts **3**, via the intermediate $Cp^*_2Ta(H)(HC{\equiv}CMe)$, to the hydrido propenylidene species $Cp^*_2Ta(H)[{=}C{=}C(H)Me]$ (**4**). Butadiene reacts with **2** to give sequentially $Cp^*_2Ta(H)(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)$ (**8**), $Cp^*_2Ta(H)[\eta^2\text{-}CH_2{=}C{=}C(H)Me]$ (**9**), $Cp^*_2Ta(H)[{=}C{=}C(H)Et]$ (**10**), and $Cp^*_2Ta(H)(MeC{\equiv}CMe)$ (**11**). **9** exists in the form of two geometrical isomers in which the allene methyl substituent lies in the equatorial coordination plane of the $[Cp^*_2Ta]$ fragment. Mechanistic studies have revealed the importance of β-H elimination from sp^2-hybridized carbon, allene roll, and 1,2-hydrogen shift processes. Treatment of $Cp^*_2Ta(H)({=}C{=}CH_2)$ with excess $CH_2{=}PMe_3$ leads to the formation of higher order linear-chain vinylidene homologues $Cp^*_2Ta(H)[{=}C{=}C(H)R]$ (R = Me, Et). A mechanism involving the intermediacy of vinylidene species and the migration of σ-alkenyl groups to a metal-bound methylene is proposed for the Fischer–Tropsch hydrocarbon-chain-lengthening process.

Introduction

Rearrangements of unsaturated hydrocarbons at transition-metal centers are of fundamental importance in a number of catalytic processes such as isomerization,[1] oligomerization[1c,2] and polymerization[3] and in stoichiometric transformations employed in organic synthesis.[3,4] The mechanisms of some elementary processes such as 1,2-hydrogen and alkyl shifts to alkylidenes,[5] olefin insertion[6,7] and β-elimination from sp^3-hybridized[6,7] and sp^2-hybridized[8] carbon centers have been conveniently studied for bent metallocene derivatives from groups 3 and 5. We report herein some extensions of those studies, investigations of the reactivity of some simple conjugated dienes with $Cp^*_2TaH_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$). The kinetic stability afforded these compounds by the two sterically demanding pentamethylcyclopentadienyl ligands has allowed us to isolate a number of unusual intermediates and products: inter alia η^3-allyl, hydrido η^2-butadiene, hydrido η^2-methylallene, and hydrido η^1-alkenylidene derivatives of permethyltantalocene. The interconversions of these compounds are exceptionally clean, and their mechanisms have been explored. In the course of our investigations of their chemical reactivity, we discovered facile carbon–carbon coupling for vinyl–methylene derivatives. Since the resultant allyl then enters this same manifold of rearrangements, it occurred to us that the $Cp^*_2TaH({=}C{=}CHR)$ systems could provide a clear-cut example of a popular model[12,16] for the chain-lengthening/homologation steps in methylene polymerization such as for Fischer–Tropsch (FT) synthesis of hydrocarbons.

Numerous model studies for homogeneous systems[9] support the basic tenets of the mechanism proposed by Brady and Pettit[10] in which surface-bound methylidene units insert into the M–H and M–C bonds of surface hydride and alkyl groups (Scheme Ia). These studies do not, however, exclude the possibility of additional C–C coupling processes. Recently, evidence has been presented for the existence of vinylidene species on the surface of FT cata-

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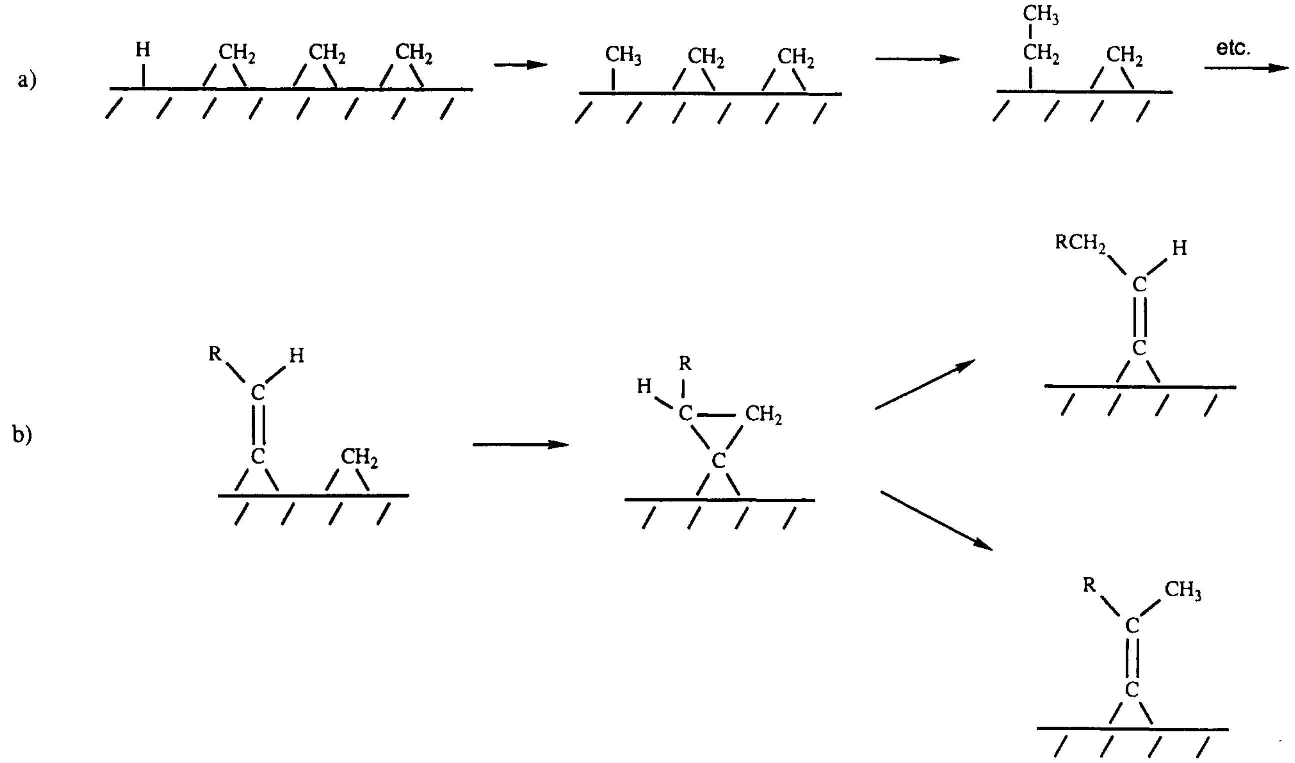
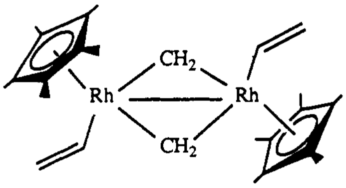
Scheme I



lysts.[11] Subsequently, a mechanism for the intermediacy of iron vinylidene species in hydrocarbon chain lengthening and branching was forwarded by McCandlish.[12] A key step in this mechanism is the addition of methylene to vinylidene to afford a cyclopropylidene species (Scheme 1b). These postulates have been tested by Hoel, who has shown that the bridging ethylidene ligand in the model compound $[CpFe(CO)_2]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ reacts with CH_2N_2 in the presence of a copper catalyst to give a diiron μ-cyclopropylidene complex.[13] Hydrocarbon chain lengthening, however, is found to occur only by protonation/deprotonation cycles[14] and results in exclusive formation of the *branched* hydrocarbon chain, in contrast to the predominant linear chain growth observed for FT synthesis.[15] Under thermal or photolytic conditions, rearrangement of the cyclopropylidene ligand to coordinated allene occurs. These results led the authors to conclude that the chemistry of cyclopropylidene in the soluble diiron system is not necessarily the same as that which could occur on heterogeneous FT catalysts. A modified version of the McCandlish mechanism, favoring the intermediacy of alkylidene species, has since been proposed by Joyner,[16] and recent synthesis studies by Maitlis and co-workers[17] reveal that the divinylbis(μ-methylene)dirhodium complex (1)



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undergoes facile coupling of vinyl and methylene to give mostly propene, along with smaller amounts of C_2 and C_4 hydrocarbons. Thus, the recent evidence suggests that σ-alkenyls may provide a chain-carrying role for the FT polymerization process.

Herein we report that the hydrido ethenylidene complex $Cp^*_2TaH({=}C{=}CH_2)$, which is in equilibrium with the less stable ethenyl derivatives $[Cp^*_2TaCH{=}CH_2]$, reacts cleanly with an excess of the methylene-transfer reagent $CH_2{=}PMe_3$, leading to sequential generation of higher order vinylidene hydride homologues.

Results and Discussion

1. Reaction of $Cp^*_2TaH_3$ with Allene. (a) Synthesis and Characterization of $Cp^*_2Ta(\eta^3\text{-}C_3H_5)$ (3). Treatment of $Cp^*_2TaH_3$ (2) with excess allene at 80 °C in benzene or toluene rapidly gives a deep red solution of the allyl complex $Cp^*_2Ta(\eta^3\text{-}C_3H_5)$ (3) (eq 1). The reaction

$$\underset{2}{Cp^*_2TaH_3} + CH_2{=}C{=}CH_2 \xrightarrow{\Delta} \underset{3}{Cp^*_2Ta(\eta^3\text{-}C_3H_5)} + \begin{cases} H_2 \\ CH_2{=}CHMe \end{cases} \tag{1}$$

$$Cp^*_2TaCl_2 + 2C_3H_5MgBr \xrightarrow{Et_2O} \underset{3}{Cp^*_2Ta(\eta^3\text{-}C_3H_5)} + 2MgBrCl \tag{2}$$

is accompanied by liberation of H_2 and formation of propene, behavior similar to that observed in related reactions between $Cp^*_2NbH_3$ and olefins.[7a] Compound 3 can also be prepared in good yield by the reaction of $Cp^*_2TaCl_2$ with 2 equiv of allylmagnesium bromide in diethyl ether at 25 °C (eq 2). Similar reactivity of $Cp^*_2TaCl_2$ toward Grignard reagents has been exploited previously to prepare hydrido olefin and hydrido vinylidene derivatives of permethyltantalocene.[5c,18]

3 is a purple crystalline solid which is similar to appearance to the analogous niobium complex[19a] and the

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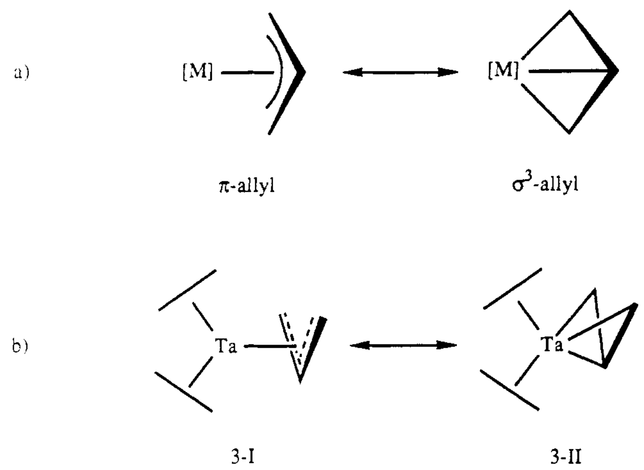
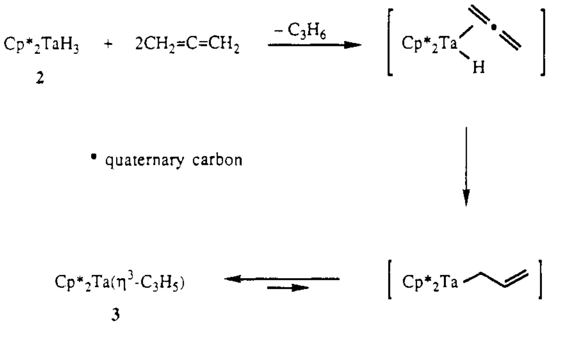


Figure 1. (a) Diagrammatic representation of the two extreme forms of bonding in the η^3-C_3H_5 ligand. (b) π-Allyl (I) and σ^3-allyl (II) forms for the η^3-C_3H_5 ligand in 3.

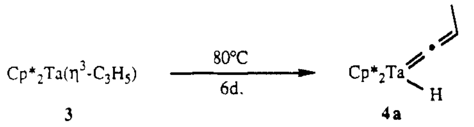
closely related cyclopentadienyl compounds $Cp_2M(\eta^3$-$C_3H_5)$ ($Cp = C_5H_5$; M = Nb, Ta).[20] However, its NMR data reveal some notable differences which suggest that the tantalum–allyl interaction is best described as a tantalabicyclobutane (Figure 1). The ^{1}H NMR spectrum (500 MHz) in benzene-d_6 (Table I) exhibits doublet of doublets at δ 2.17 and 0.40 attributable to the syn and anti hydrogens of a static η^3-allyl ligand with a $^2J_{HH}$ coupling of 7.6 Hz; the remaining allylic hydrogen is observed as a triplet of triplets at δ −0.13. These shifts, in particular those for the anti and allylic hydrogens, are more consistent with hydrogen attached to metal-bound sp^3-hybridized carbon (for comparative purposes, allylic hydrogen shifts in other allyl complexes are normally found in the range δ 4–6.5[21a]). Furthermore, a geminal (syn–anti) coupling of 7.6 Hz is well outside the range (0–3 Hz) typically observed for geminal sp^2 olefinic hydrogens[26] (coupling is usually unobservable for most allylic complexes where considerable sp^2 character predominates, e.g., $[Pd(\eta^3$-$C_3H_5)Cl]_2$[27]). The ^{13}C NMR spectrum for 3 lends further support to there being considerable sp^3 character in the ligand carbon atoms, most notably unusually high field shifts[23] for the terminal and central carbons (δ 56.1 and 42.6) and relatively low $^1J_{CH}$ coupling constants (147–149 Hz).[24,25] Thus, the NMR data are consistent with a significant contribution to the metal–allyl bonding from the M–C(sp^3) interactions of resonance form **3-II** (Figure 1) in which the metal allyl is best described as a metallabicyclobutane or σ^3-allyl moiety.

The formation of 3 may be rationalized according to eq 3 in which a coordinated allene inserts into the Ta–H bond to give a 16-electron σ-allyl species which then rapidly rearranges to the thermodynamically preferred η^3-allyl complex. The proposed mechanism is supported by deuterium-labeling experiments, in which 2 reacts with $CD_2{=}C{=}CD_2$ to yield $CD_2{=}CHCD_2H$ and $Cp^*_2Ta(\eta^3$-$CD_2CHCD_2)$ exclusively (^{1}H NMR).



(3)

(b) Rearrangement of $Cp^*_2Ta(\eta^3$-$C_3H_5)$ (3) to $Cp^*_2Ta(H)[{=}C{=}C(H)Me]$ (4a). While stable indefinitely at or below room temperature, 3 rearranges upon prolonged warming at 80 °C in toluene-d_8 to give an orange solution containing the η^1-propenylidene complex **4a** (90%, ^{1}H NMR) (eq 4). **4a** may be isolated in the form of colorless crystals by cooling a petroleum ether extract of the dried product mixture to −50 °C.



(4)

Its ^{1}H NMR spectrum (400 MHz) in benzene-d_6 (Table I) gives a singlet at δ 1.93 due to the hydrogens of equivalent Cp* ligands, suggesting that the methyl and hydrogen substituents of the propenylidene ligand lie in the equatorial coordination plane, as expected for maximum π-overlap of the frontier orbitals of $[Cp^*_2TaH]$ and $[C{=}C(H)Me]$. The methyl substituent occurs as a doublet at δ 1.92 with a $^3J_{HH}$ coupling of 6.9 Hz to the propenylidene hydrogen. The latter gives a quartet of doublets resonance at δ 6.77 with an additional long-range $^4J_{HH}$ coupling of 2.3 Hz to the tantalum hydride ligand. This coupling is too small to be resolved in the broadened resonance at δ −0.01 ($\Delta_{1/2} \simeq 8$ Hz) attributable to Ta-*H*, but its origin was confirmed by a homonuclear ^{1}H–^{1}H decoupling experiment. The broadening of the hydride signal is likely due to the proximity of the hydride to the quadrupolar ^{181}Ta nucleus.

The ^{13}C NMR spectrum possesses signals consistent with a metal–vinylidene moiety:[28] an apparent triplet at δ 348.4 is assignable to the quaternary carbon of the propenylidene ligand. The triplet signal arises from small, fortuitously similar two-bond ^{13}C–^{1}H couplings of ca. 5 Hz to the metal hydride and propenylidene hydrogen. The β-carbon of the propenylidene ligand resonates at δ 120.9 as a doublet of quartets [$^1J_{CH}$ = 152.6, $^2J_{CH}$ = 6.7 Hz] with the long-range quartet coupling attributable to the hydrogens of the propenylidene methyl substituent. Finally, a quartet of doublets at δ 18.3 is assigned to the methyl carbon of the

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(22) Mann. B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

(23) Allylic carbons are usually found in the range δ 110–130. See refs 21a and 22.

(24) Typically 150–160 Hz for $^1J_{CH}$ at sp^2-hybridized carbon. See ref 25.

(25) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 333.

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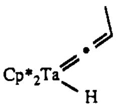
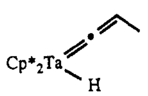
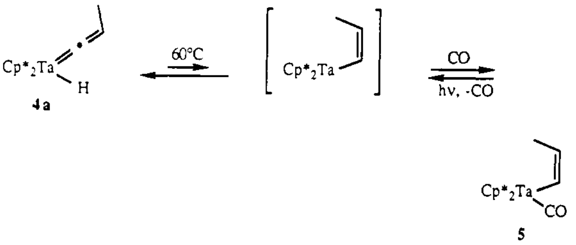
propenylidene ligand with a $^2J_{CH}$ coupling of 2.1 Hz to the propenylidene hydrogen. The IR spectrum of **4a** reveals an absorption at 1775 cm^{-1} due to ν(Ta–H). However, unlike for the ethenylidene complex, $Cp^*_2Ta(H)(=C=CH_2)$,[5c] a band due to ν(C=C) is not apparent.

Of the two possible isomeric forms, **4a** and **4b**, which agree with the equivalence of the Cp* ligands, only **4a** is formed. Consistently, the reaction of 4 with carbon


4a


4b

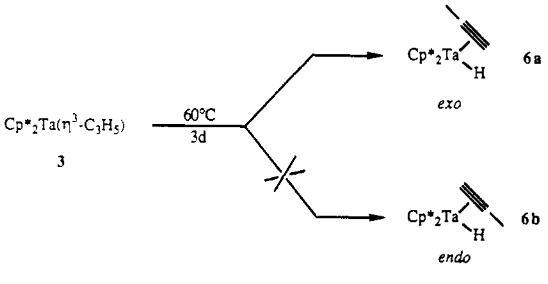
monoxide at 60 °C for 24 h gives the green (*Z*)-propenyl complex **5**[29] arising by insertion of the propenylidene ligand into the tantalum–hydrogen bond to afford a 16e$^-$ propenyl intermediate which is trapped by carbon monoxide (eq 5).



(5)

Similar reactivity toward CO has been observed previously for the parent ethenylidene complex $Cp^*_2Ta(H)(=C=CH_2)$.[5c] The ^{1}H NMR data for the propenyl ligand confirm a cis 1,2-substitution of the double bond; in particular, a 12.6-Hz $^3J_{HH}$ coupling between the vinylic hydrogens is comparable with the 12.1-Hz cis coupling observed in $Cp^*_2Ta(CH=CH_2)(CO)$ ($^3J_{HH}$ coupling between *trans*-vinylic hydrogens are usually found in the range 18–21 Hz[5c,8,19a]). UV irradiation of **5** with a medium-pressure mercury lamp regenerates **4**, demonstrating the reverse α-H elimination from sp^2-hybridized carbon.

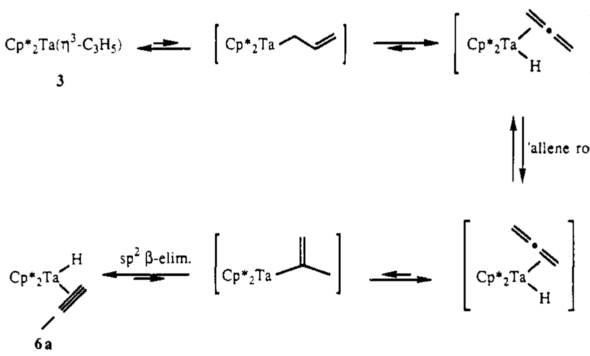
(c) Mechanism of the Formation of $Cp^*_2Ta(H)(=C=C(H)Me)$ (4a) from 3. An intermediate, formed during the conversion of **3** to **4a**, has been identified as the 1-propyne complex $Cp^*_2Ta(H)(HC\equiv CMe)$ (**6a**) by NMR spectroscopy. **6a** is only present in low concentration, but its formation may be optimized by warming **3** at 60 °C for 3 days, resulting in a concentration of **6a** amounting to approximately 18% of the combined permethyltantalocene components of the reaction mixture. Once again, a single isomer only is observed (eq 6) for which exo geometry (**6a**)



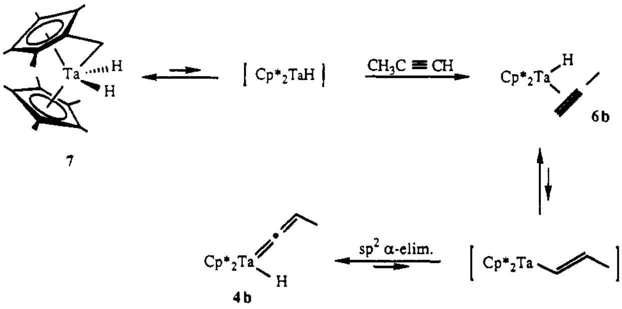
(6)

is favored on the basis of couplings observed in the high-field ^{1}H NMR spectrum. In particular, a doublet of quartets resonance at δ 7.79 is assignable to the acetylenic hydrogen, which couples with a magnitude of 7.6 Hz to the tantalum hydride ligand.[30] Doublet resonances at δ 2.67 ($^4J_{HH}$ = 1.5 Hz) and 0.60 ($^3J_{HH}$ = 7.6 Hz) are attributable to the propyne methyl substituent and metal hydride. A remaining singlet at δ 1.80 is due to the methyl hydrogens of equivalent Cp* ligands. The preferential formation of the exo isomer may be rationalized according to Scheme II. The mechanism is comprised of interconversion of hydrido allene isomers and β-H elimination from the sp^2 carbon of the 16e$^-$ 2-propenyl intermediate.

Scheme II



Scheme III



The interconversion of metal allene isomers by a low-energy "allene roll" mechanism[31] whereby the metal fragment migrates to the orthogonal π-orbital of the adjacent carbon–carbon double bond is well precedented. Further evidence for the formation and interconversion of the hydrido allene species postulated here is provided by the interconversion of isomers of an analogous methylallene complex from the reaction of **2** with butadiene (vide infra). Although β-H elimination from sp^2 carbon has been described previously,[8] of particular note here is the competition for elimination of hydrogen from sp^2- and sp^3-hybridized carbons of the 2-propenyl ligand with the product of the β-H elimination from the sp^2 carbon, yielding the more stable products in this case. Consistently, deuterium-labeling studies showed that **3**-d_4, $Cp^*_2Ta(\eta^3\text{-}CD_2CHCD_2)$, prepared via the reaction of $Cp^*_2TaH_3$ with allene-d_4 is converted to $Cp_2{}^*TaD(DC\equiv C(CD_2H))$ (>95% ^{1}H and ^{2}H NMR).

Irradiation of a solution containing **6a** leads to formation of the endo isomer **6b**.[30] The ^{1}H NMR spectrum (Table I) of **6b** bears close similarity to that of **6a**, with the exception that coupling between the propyne hydrogen and metal hydride is no longer observed. This would appear to be consistent with the endo geometry for **6b** in which the methyl substituent is directed "inward" toward the metal hydride ligand. Such an arrangement is expected

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[29] **5** has been characterized by ^{1}H NMR spectroscopy only. A small amount of a second species is also observed in the mixture, believed to result from further reaction of **5** with CO(g).

[30] Couplings of similar magnitude are observed between the endo olefinic hydrogens and the hydride ligand in $Cp_2M(C_2H_3R)H$ complexes. See ref 7.

[31] Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

[32] A 50:50 mixture of **6a** and **6b** is obtained, which may represent an equilibrium mix at room temperature.

Table I. NMR and IR Data

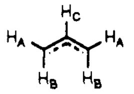
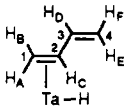
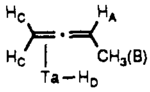
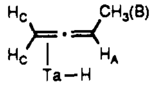
compd		IR, cm^{-1}	assignment	NMR (chem shift, multiplicity, coupling consts, Hz) ^{1}H	^{13}C
Cp$_2$*Ta(η^3-C$_3$H$_5$)	**3**		$C_5(\mathit{CH}_3)_5$	1.56, s	12.4, q, $J_{CH} = 126$
				1.74, s	11.8, q, $J_{CH} = 126$
			$C_5(CH_3)_5$		98.0, s
					103.1, s
				2.17, dd, $J_{AB} = 7.6$, $J_{AC} = 10.2$	
				0.40, dd, $J_{BA} = 7.6$, $J_{BC} = 14.5$	
				−0.13, tt, $J_{CA} = 10.2$, $J_{CB} = 14.5$	
			$\mathit{CH}_2CH\mathit{CH}_2$		42.6, dd, $J_{CH} = 148, 147$
			$CH_2\mathit{C}HCH_2$		56.1, d, $J_{CH} = 149$
Cp$_2$*Ta(H)(=C=C-(H)Me)	**4**	1775 ν(Ta-H)	$C_5(\mathit{CH}_3)_5$	1.93, s	12.1, dq, $J_{CH} = 127, 1.8$
			$\mathit{C}_5(CH_3)_5$		105.4, s
			CH_3	1.92, d, $^3J_{HH} = 6.9$	18.3, dq, $J_{CH} = 126, 2.1$
			CH	6.77, qd, $^3J_{HH} = 6.9$, $^4J_{HH} = 2.3$	120.9, dq, $J_{CH} = 152.6, 6.7$
			$Ta{=}\mathit{C}{=}C$		348.4, app. t, $J_{CH} \simeq 5$
			$Ta{-}\mathit{H}$	−0.01, s (bd)	
Cp$_2$*Ta(H)(HC≡CMe)	**6a**		$C_5(\mathit{CH}_3)_5$	1.80, s	
			CH	7.79, dq, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.5$	
			CH_3	2.67, d, $^4J_{HH} = 1.5$	
			$Ta{-}\mathit{H}$	0.60, d, $^3J_{HH} = 7.6$	
	6b		$C_5(\mathit{CH}_3)_5$	1.78, s	
			CH	7.58, q, $^4J_{HH} = 1.7$	
			CH_3	2.94, d, $^4J_{HH} = 1.7$	
			$Ta{-}\mathit{H}$	0.25, s (bd)	
Cp$_2$*Ta(H)(η^2-CH$_2$=CHCH=CH$_2$)	**8**	1800 ν(Ta—H) 1590 ν(C=C)	$C_5(\mathit{CH}_e)_5$	1.63, s	11.2, q, $J_{CH} = 127$
				1.75, s	12.0; q, $J_{CH} = 127$
			$\mathit{C}_5(CH_3)_5$		104.0, s (overlapping)
				H_A 0.20, dd, $J_{AB} = 7.6$, $J_{AC} = 10.3$	
				H_B −0.04, dd, $J_{BA} = 7.6$, $J_{BC} = 12.0$	
				H_C 1.63, (obscured by $C_5(\mathit{CH}_3)_5$)	
				H_D 6.22, ddd, $J_{DC} = 9.3$, $J_{DE} = 16.6$, $J_{DF} = 9.5$	
				H_E 5.25, ddd, $J_{EC} = 1.2$, $J_{ED} = 16.6$, $J_{EF} = 2.7$	
				H_F 4.74, ddd, $J_{FC} = 1.0$, $J_{FD} = 9.5$, $J_{FE} = 2.7$	
			C_1		25.1, t, $J_{CH} = 144.0$
			C_2		39.4, d, $J_{CH} = 152.6$
			C_3		153.5, d, $J_{CH} = 145.3$
			C_4		101.4, t, $J_{CH} = 150.8$
			$Ta{-}\mathit{H}$	−1.78, s (bd)	
Cp$_2$*(H)(η^2-CH$_2$=C=C(H)Me)	**9a**, **9b**	1765, 1820 ν(Ta—H) 1665 ν(C=C)			
Cp$_2$*Ta(H)(η^2-CH$_2$=C=C(H)Me)	**9a**		$C_5(\mathit{CH}_3)_5$	1.71, s	11.3, q, $J_{CH} = 126$
			$\mathit{C}_5(CH_3)_5$		104.8, s
				H_A 7.71, qtd, $J_{AB} = 6.1$, $J_{AC} = 2.9$, $J_{AC} = 0.8$	
				$CH_3(B)$ 2.33, dt, $J_{BA} = 6.1$, $J_{BC} = 2.7$	
				H_C −0.25, dq, $J_{CA} = 2.9$, $J_{CB} = 2.7$	
			$\mathit{C}H_2{=}C{=}C(H)Me$		4.7, t, $J_{CH} = 145.3$
			$CH_2{=}\mathit{C}{=}CH(Me)$		183.8, s
			$CH_2{=}C{=}\mathit{C}H(Me)$		128.2, d, $J_{CH} = 158.7$
			$CH_2{=}C{=}CH(\mathit{Me})$		21.3, qd, $J_{CH} = 125.7, 7.3$
			$Ta{-}H$	−1.12, s (bd)	
	9b		$C_5(\mathit{CH}_3)_5$	1.70, s	11.3, q, $J_{CH} = 126$
			$\mathit{C}_5(CH_3)_5$		104.8, s
				H_A 6.56, qt, $J_{AB} = 6.1$, $J_{AC} = 3.2$	
				$CH_3(B)$ 2.42, dt, $J_{BA} = 6.1$, $J_{BC} = 2.2$	
				H_C −0.34, dq, $J_{CA} = 3.2$, $J_{CB} = 2.2$	
			$\mathit{C}H_2{=}C{=}C(H)Me$		3.6, td, $J_{CH} = 145.3, 7.3$
			$CH_2{=}\mathit{C}{=}C(H)Me$		182.4, s
			$CH_2{=}C{=}\mathit{C}(H)Me$		124.1, d, $J_{CH} = 153.8$
			$CH_2{=}C{=}C(H)\mathit{Me}$		25.2, dq, $J_{CH} = 124.5, 8.5$
			$Ta{-}H$	−1.59 s (bd)	
Cp$_2$*Ta(H)(=C=C-(H)Et)	**10**	1795 ν(Ta—H)	$C_5(\mathit{CH}_3)_5$	1.95, s	12.1, q, $J_{CH} = 127$
			$\mathit{C}_5(CH_3)_5$		105.5, s
			CH_3	0.99, t, $^3J_{HH} = 15.1$	15.3, q, $J_{CH} = 124.5$
			CH_2	obscured by $C_5(\mathit{CH}_3)_5$	26.8, t, $J_{CH} = 125.7$
			CH	6.27, dt, $^3J_{HH} = 7.1$, $^4J_{HH} = 1.7$	130.4, d, $J_{CH} = 152.6$
			$Ta{=}\mathit{C}{=}C$		346.2, s (bd)

Table I (Continued)

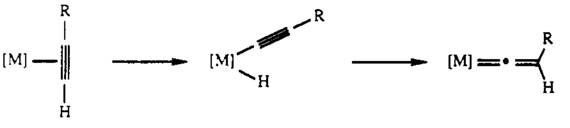
compd		IR, cm^{-1}	assignment	NMR (chem shift, multiplicity, coupling consts, Hz) ^{1}H	^{13}C
$Cp_2^*Ta(H)(MeC{\equiv}CMe)$	11	1790 ν(Ta—H)	$C_5(CH_3)_5$	1.77, s	11.6, q, J_{CH} = 126
		1750 ν(C≡C)	$C_5(CH_3)_5$		106.6, s
			CH_3	2.78, s	
			CH_3	2.52, s	
			CH_3 (en)		19.6, qd, J_{CH} = 125.1, 6.1
			CH_3 (exo)		15.1, q, J_{CH} = 125.7
			≡C—		148.9, s
			≡C—		142.1, s
			Ta—H	0.45, s (bd)	

to be favored thermodynamically as models show that the central equatorial coordination site represents the sterically least hindered position. Attempts to prepare **6a** or **6b** from **2** and propyne at 80 °C led only to intractable products.

On the other-hand, cyclometallated $Cp^*(C_5Me_4(CH_2))TaH_2$ (**7**)[33] provides an incipient source of $[Cp^*_2TaH]$ at room temperature via hydrogen migration from metal to ring methylene, and its reaction with propyne at 25 °C does indeed afford the endo isomer **6b** (Scheme III).

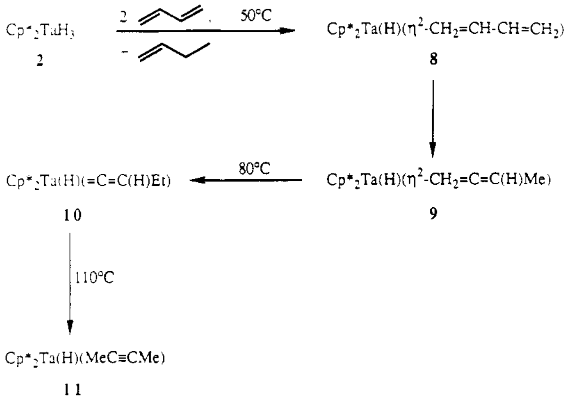
6b also undergoes a similar transformation to a vinylidene, but interestingly now exclusively to the complementary isomer **4b**! A likely mechanism for this process is shown in Scheme III. Here, the 16e$^-$ hydrido species $[Cp^*_2TaH]$ is trapped by propyne to give the thermodynamically favored endo isomer **6b**. Insertion of the propyne ligand into the tantalum hydride bond affords the 16e$^-$ 1-propenyl intermediate which can then undergo α-H elimination from the sp^2-hybridized carbon of the propenyl ligand to give **4b**. α-H elimination from sp^2 carbon has been demonstrated previously[5c] and in the elimination of CO from **4a**. Thus, the distinct pathways followed in the formation of **4a** and **4b** from **6a** and **6b**, respectively, suggest that **6a** and **6b** (or for that matter any intermediates generated during the transformation) do not equilibrate thermally.

The conversion of **6a** to **4a** at 60 °C is similar to rearrangements of terminal alkyne to metal vinylidene ligands previously observed for a variety of complexes.[34] The mechanism attending this transformation is not well understood, however. Of the two steps indicated in eq 7, the oxidative addition of an alkyne C–H bond to a metal to give hydrido acetylide species has been observed.[35] However, the conversion of hydrido acetylide to vinylidene via a concerted intramolecular 1,3-hydrogen shift seems unlikely since calculations indicate a prohibitively large barrier to such a process.[36] A substantial charge localization at the β-carbon of the acetylide ligand[37] would suggest that deprotonation/protonation to give intermediate acetylides presents a more reasonable alternative. We have been unable to identify any acetylide species during the conversion of **6a** to **4a**, and attempts to prepare such complexes by metathesis of $Cp^*_2MCl_2$ [M = Nb, Ta] with LiC≡CR[38] (R = Me, Ph) have proved unsuccessful. An additional complication is also apparent in the system under study here, since deuterium labels are found to scramble into the ring methyl sites of **4a** in addition to the metal hydride and β-hydrogen and methyl substituents of the propenylidene ligand. Thus, the available data do not allow us to clarify the mechanistic pathway beyond the formation of **6a** and appear to be complicated by ring methyl activation processes.



(7)

2. Reaction of $Cp^*_2TaH_3$ with Butadiene. The reaction of **2** with 1,3-butadiene in benzene or toluene affords sequentially $Cp^*_2Ta(H)(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)$ (**8**), $Cp^*_2Ta(H)(\eta^2\text{-}CH_2{=}C{=}C(H)Me)$ (**9**), $Cp^*_2Ta(H)({=}C{=}C(H)Et)$ (**10**), and $Cp^*_2Ta(H)(MeC{\equiv}CMe)$ (**11**) (eq 8).



(8)

Compounds **8**–**11** arise by rearrangement of the coordinated C_4H_6 fragment and bear close similarities to the intermediates both isolated or postulated in the reaction of **2** with allene.

(a) Synthesis and Characterization of $Cp^*_2Ta(H)(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)$ (8). Spectroscopic data for **8** are given in Table I. The ^{1}H NMR spectrum (400 MHz) in benzene-d_6 consists of singlets at δ 1.63 and 1.75 due to the methyls of inequivalent Cp* ligands, a broad hydride resonance at δ −1.78, and six discrete multiplets at δ −0.04, 0.20, 1.63, 4.74, 5.25, and 6.25 attributable to the hydrogens of coordinated butadiene. The multiplet at δ 1.63 was shown by a homoscalar-correlated 2D (COSY) ^{1}H NMR spectrum (Figure 2) to lie beneath the methyl resonance of one of the C_5Me_5 ligands.

The chemical shifts of the butadiene hydrogens are consistent with coordinated (δ −0.04, 0.20, and 1.63) and noncoordinated (δ 4.74, 5.25, and 6.25) olefinic bonds. Moreover, trans, cis, and geminal ^{1}H–^{1}H coupling constants of 16.6, 9.5, and 2.7 Hz, respectively, accompanying the high-frequency signals are typical for free alkenes.[24]

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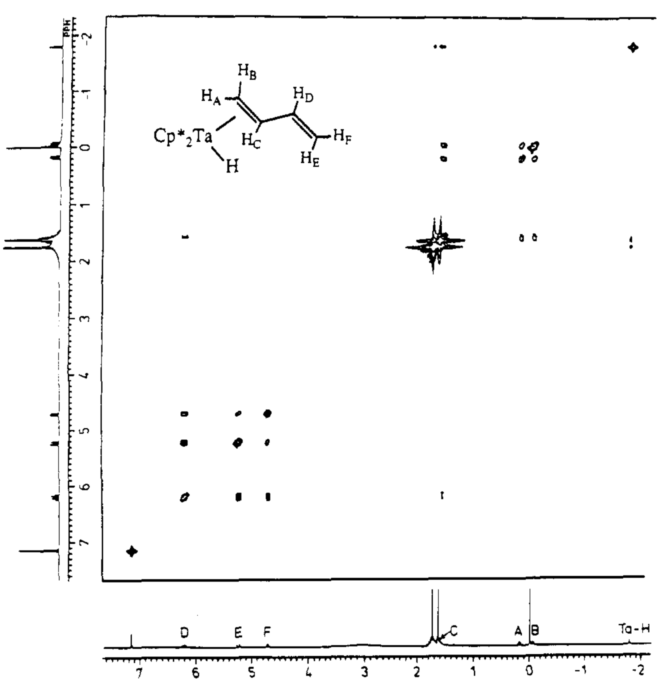
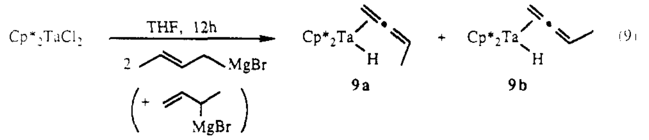


Figure 2. Homoscalar-correlated 2D (COSY) 400-MHz ^{1}H NMR spectrum of 8.

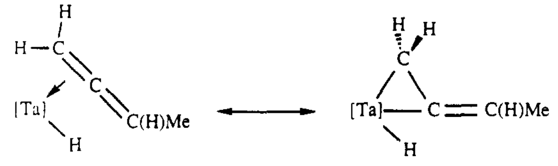
The ^{13}C NMR spectrum exhibits signals at δ 25.1 (t, $^1J_{CH}$ = 144.0 Hz) and 39.4 (d, $^1J_{CH}$ = 152.6 Hz) due to the metal-bound carbons of the butadiene ligand, and resonances at δ 101.4 (t, $^1J_{CH}$ = 150.8 Hz) and 153.5 (d, $^1J_{CH}$ = 145.3 Hz) are attributable to the carbons of the uncoordinated double bond. The latter is also supported by a strong absorption at 1590 cm^{-1} in the IR spectrum due to ν(C=C). Thus, 8 is formulated as an η^2-butadiene complex. It has not proved possible to establish unequivocally whether endo or exo geometry prevails for the coordinated olefin. However, an X-ray structural analysis on Cp*$_2$Nb(H)(CH$_2$=CHPh)[39] and our observations on related permethylmetallocene olefin derivatives[6,18,19b] suggest that the endo form will be favored sterically. Also, endo geometry for 8 is supported by the observation of a small coupling between Ta–*H* and the obscured hydrogen H$_c$ in the 2D (COSY) ^{1}H NMR spectrum.[40] In contrast, coupling between Ta–*H* and the methylene hydrogens H$_a$ and H$_b$ is not observed. While η^2-butadiene species have been isolated for late transition-metal systems[41] and have been postulated to mediate a variety of transformations involving Cp$_2$Zr(C$_4$H$_6$),[42] to our knowledge 8 represents the first isolable example of an early transition-metal η^2-butadiene complex.

(b) Synthesis and Characterization of Cp*$_2$Ta(H)(η^2-CH$_2$=C=(H)Me) (9). Compound 9 was not formed in sufficiently high concentration to allow its isolated from the reaction mixture. Therefore, an alternative method of preparation was investigated. Treatment of Cp*$_2$TaCl$_2$ with 2 equiv of *trans*-crotylmagnesium bromide, prepared from commercially available 1-bromobut-2-ene (containing ~20% 3-bromobut-1-ene), gave a mixture of two isomers corresponding to compound 9 in 66% yield. The two components have been characterized as isomers **9a** and **9b** of a hydrido methylallene complex (eq 9).

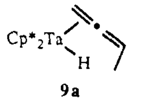


Measurement of peak intensities in the ^{1}H NMR spectrum (400 MHz, benzene-d_6) shosed that **9a** and **9b** are formed in the ratio 62:38. Each compound gives rise to only one resonance in the ^{1}H NMR spectrum (δ 1.71 (**9a**) and 1.70 (**9b**)) attributable to the methyl hydrogens of equivalent Cp* ligands for each isomer. Thus, the tantalum atom must be bound to the unsubstituted double bond of the methylallene ligand with the methyl substituent lying in the equatorial plane of the [Cp*$_2$Ta] moiety.

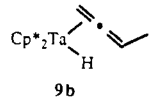
The remaining multiplets were assigned according to their peak intensities and extensive ^{1}H–^{1}H decoupling experiments. In particular, for isomer **9a**, a multiplet at δ 7.71 is attributable to the unique β-hydrogen (H$_A$) of the methylallene ligand with couplings to the methyl (6.1 Hz), methylene (2.9 Hz), and hydride (0.8 Hz) hydrogens, respectively. A doublet of quartets resonance at δ –0.25 ($^4J_{HH}$ = 2.9, $^5J_{HH}$ = 2.7 Hz) is assignable to the hydrogens (H$_c$) of the tantalum-bound methylene group, while Ta–*H* occurs as a quadrupolar-broadened resonance at δ –1.12. The methyl substituent gives a doublet of triplets resonance at δ 2.33 ($^3J_{HH}$ = 6.1, $^5J_{HH}$ = 2.7 Hz). The ^{13}C NMR spectrum for **9a** shows a characteristic singlet resonance at δ 183.8 due to the quaternary carbon of the methylallene ligand. This shift is to a frequency lower than that usually observed for free allenes (typically δ 200–215[24]) and is consistent with quaternary carbon shifts of other transition-metal allene complexes.[22] A triplet resonance at δ 4.7 ($^1J_{CH}$ = 145.3 Hz) is assigned to the tantalum-bound methylene carbon, and a doublet resonance at δ 128.2 ($^1J_{CH}$ = 158.7 Hz) is consistent with the remote sp^2-hybridized carbon of the methylallene ligand. Finally, the carbon of the methyl substituent resonates as a quartet of doublets at δ 21.3 ($^1J_{CH}$ = 125.7, $^2J_{CH}$ = 7.3 Hz), the smaller doublet value arising due to two-bond coupling to H$_A$. Isomer **9b** exhibits closely analogous ^{1}H and ^{13}C NMR data (Table I). The most notable features of the NMR data for **9a** and **9b** are the low-frequency shifts of the metal-bound methylene carbon (δ 4.7 (**9a**) 2.4 (**9b**)) and hydrogens (δ –0.25 (**9a**), –0.34 (**9b**)) along with reduced ^{13}C–^{1}H coupling constants of 145.3 Hz. These data are consistent with considerable sp^3 character in the metal-bound carbon atoms, suggesting a significant contribution to the metal–allene bonding from the ethylenetantalacyclopropane resonance form, 9–**II**.



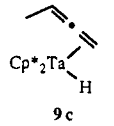
9-I 9-II



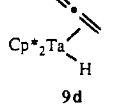
9a



9b



9c



9d

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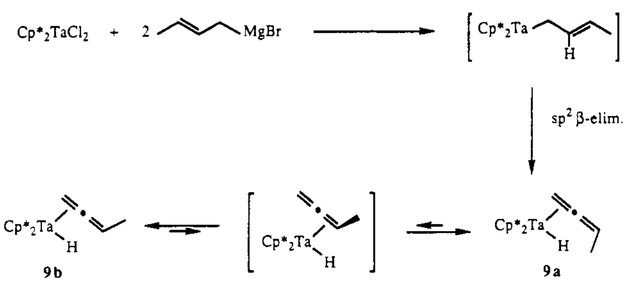
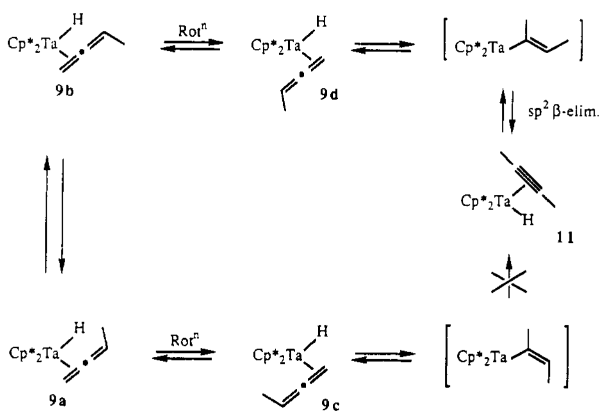
Scheme IV



Scheme V

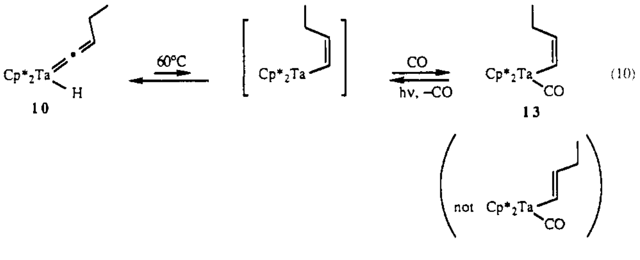


Although X-ray data are not available for early transition-metal allene complexes, structural determinations on related middle-to-late transition-metal complexes do indeed show a considerable bending of the bound allene ligand.[43] It might be anticipated that this effect will be even more pronounced for a π-adduct of a low-valent, early transition metal such as Ta^{III}.

Of the four possible methylallene ligand orientations with respect to the metal hydride (below), nuclear Overhauser effect (NOE) experiments rule out **9c** and **9d**. In particular, irradiation of the hydrogens of the allene methyl substituent lead in the case of one isomer to considerable enhancement of the metal hydride resonance, consistent with the proximal hydride–methyl arrangement of **9a**. The methyl resonance of the second isomer did not lead to enhancement of the hydride signal. Rather, a significant nuclear Overhauser effect was observed between the hydride and unique hydrogen of the methylallene ligand, consistent with isomer **9b**. The preferential formation of **9a** and **9b** may be rationalized, for the same reasons outlined earlier, on steric grounds. However, other orientations of the methylallene ligand appear to be energetically accessible since **9a** is converted slowly to **9b** (weeks at room temperature). A mechanism for the formation and interconversion of **9a** and **9b** is shown in Scheme IV, which is dependent upon β-H elimination from the sp^2 carbon of a $16e^-$ σ-crotyl species followed by an allene roll process which serves to equilibrate **9a** and **9b**.[44]

(c) Synthesis and Characterization of $Cp^*{}_2Ta(H)(=C=C(H)Et)$ (10). The third major product formed sequentially from the reaction of **2** with butadiene is the butenylidene complex $Cp^*{}_2Ta(H)(=C=C(H)Et)$ (**10**). A single isomer is obtained whose ^1H and ^{13}C NMR data (Table I) closely resemble those of the exo propenylidene complex **4a**.

The reaction of **10** with CO(g) (eq 10) allowed us to confirm exo geometry for **10** through observation of the butenyl insertion product (**12**). ^1H NMR resonances at δ 6.90 (dt, $^3J_{HH}$ = 12.6, $^3J_{HH}$ = 1.5 Hz) and 6.09 (dt, $^3J_{HH}$ = 12.6, 6.4 Hz) due to the α- and β-hydrogens, respectively, of the butenyl ligand revealed a cis $^3J_{HH}$ coupling of 12.6 Hz, indicating that **13** must arise by trapping of the σ-butenyl insertion product of **10**.



Similar to the reaction of $Cp^*{}_2TaH_3$ with allene, an intermediate terminal alkyne species is observed prior to the formation of **10**. The high-field ^1H NMR data are consistent with the 1-butyne complex $Cp^*{}_2Ta(H)(HC{\equiv}CEt)$ (**13**). Although never formed in sufficiently high concentration to allow its isolation from the reaction medium, high-field ^1H NMR data revealed signals at δ 7.72 (dt. J_{HH} = 7.8, 1.5 Hz) and 0.52 (d, J_{HH} = 7.8 Hz) attributable to the terminal acetylenic hydrogen and metal hydride, respectively. By analogy with **6a**, **12** is thus assigned an exo geometry, and its formation may be rationalized by a pathway analogous to the formation of **6a** (Scheme II).

(d) Synthesis and Characterization of $Cp^*{}_2Ta(H)(MeC{\equiv}CMe)$ (11). The final product (prior to decomposition) of the reaction of **2** with butadiene is the but-2-yne complex $Cp^*{}_2Ta(H)(MeC{\equiv}CMe)$ (**11**), which is formed in 80% yield upon prolonged warming of the reaction mixture at 110 °C. **11** is conveniently prepared by treatment of **2** with 2 equivalents of but-2-yne. Preliminary data for this compound have been reported,[18] and full spectrscopic data are included in Table I. NMR and IR data are consistent with η^2-coordination of the alkyne ligand in the $[Cp^*{}_2Ta]$ equatorial plane, leading to inequivalence of the methyl substituents of the symmetrical alkyne. The ^{13}C NMR spectrum revealed a small coupling (6.1 Hz) between the hydride and one of the but-2-yne methyl carbons, presumably the methyl attached to the endo carbon of the coordinated alkyne. Singlet resonances at δ 142.1 and 148.9 are consistent with acetylenic carbons of a $2e^-$ alkyne ligand. Similar shifts are observed for related niobium derivatives[19] and are some 40 ppm lower in frequency than acetylenic carbon shifts for $4\ e^-$ alkyne ligands to tantalum.[45]

The formation of **11** at elevated temperature may be rationalized due to the accessibility of a thermodynamically less favored hydrido methylallene isomer **9d** either by an endo-to-end rotation of the coordinated methylallene ligand (as shown in Scheme V) or alternatively by ligand dissociation. According to this mechanism only **9b** will lead to **11** since the β-sp^2 hydrogen of the 2-butenyl isomer arising from **9c** is not accessible to the metal center.

3. Reaction of $Cp^*{}_2Ta(H)(=C=CH_2)$ with CH_2PMe_3. In view of the current interest in the role of

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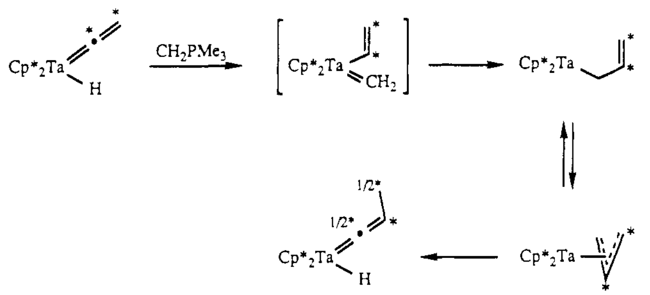
[43] (a) Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *80*, 21. (b) Shaw, B. L.; Stringer, H. A. *Inorg. Chim. Acta Rev.* **1973**, *7*, 1.

[44] The slow conversion of **9a** to **9b** does not account for the high initial concentration of **9b**, amounting to some 38% of the combined isomer concentration. This is believed to arise due to the presence of 3-bromo-1-butene in commercially available *trans*-crotyl bromide. The reaction of $Cp^*{}_2TaCl_2$ with the resultant *trans*-crotyl Grignard will generate a higher energy methylallene isomer, which, by ligand rotation and roll processes, can also lead to **9a** and **9b**.

[45] McGreary, M. J.; Gamble, A. S.; Templeton, J. L. *Organometallics* 1988, *7*, 271 and references therein.

Scheme VI

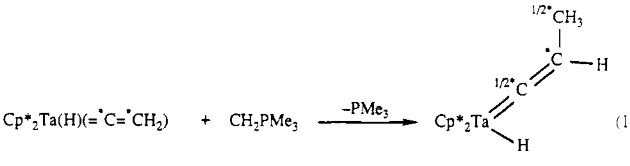


metal vinylidenes in the Fischer–Tropsch hydrocarbon-chain-lengthening process, we have examined the reactivity of hydrido vinylidene complexes with the methylene-transfer reagent, CH_2PMe_3, in order to determine if higher order vinylidene homologues result.

A mixture of $Cp^*_2Ta(H)({=}C{=}CH_2)$ and a 3-fold excess of CH_2PMe_3 was heated at 110 °C for 2 days, resulting in 40% conversion of $Cp^*_2Ta(H)({=}C{=}CH_2)$ to $Cp^*_2Ta(H)({=}C{=}C(H)Me)$ (**4b**) and liberation of PMe_3 as determined by ^1H NMR spectroscopy.[46] Significantly, only isomer **4b** is produced, readily identified by the characteristic signal of the β-vinylidene hydrogen.

Continued warming of the mixture at 110 °C led to the consumption of all the ethenylidene complex, a slight decrease in the amount of the propenylidene species, and the appearance of a triplet of doublets resonance in the vinylidene β-hydrogen region, attributable to the butenylidene complex **10a**. Prolonged heating of the mixture, while leading to an increase in the proportion of the higher order homologues, also lead to a diminution of the ring and vinylidene ligand resonances, most probably due to H/D exchange with deuteriobenzene solvent. For this reason and due to the inherent instability of the butenylidene complex at 110 °C, it did not prove possible to monitor the formation of vinylidene species beyond this stage. Nevertheless, incorporation of methylidene units into a growing vinylidene chain was apparent.

In order to gain insight into the mechanism of homologation, the reaction between $Cp^*_2Ta(H)(={}^{13}C={}^{13}C_2)$[47] and CH_2PMe_3 was monitored by ^{13}C NMR spectroscopy, resulting in a 1:2:1 distribution of the ^{13}C label between the α-, β-, and γ-sites of the propenylidene ligand (eq 11).



(11)

Such a distribution may be reasonably accounted for by formation of a symmetric allyl intermediate (according to Scheme VI), which then converts by the mechanism outlined earlier to the propenylidene complex. Consistently, as observed for the conversion of $Cp^*_2Ta(\eta^3\text{-}C_3H_5)$ to $Cp^*_2Ta(H)({=}C{=}C(H)Me)$, only a single propenylidene isomer, **4b**, is formed.

The mechanism of the formation of the allyl species is less certain, but by analogy wit the formation of $Cp^*_2Ta(CH_3)(={CH_2})$ from $Cp^*_2Ta(H)(={CH_2})$ and CH_2PMe_3,[5c] and trapping of a 16e$^-$ vinyl intermediate by methylidenetrimethylphosphorane would seem most reasonable. Similar trapping of a vinyl intermediate has also been observed in the reaction of $Cp^*_2Ta(H)({=}C{=}CH_2)$ and CO(g), giving $Cp^*_2Ta(CH{=}CH_2)(CO)$.[5c] By analogy with the methyl to methylene migration observed in the conversion of the methylmethylidene complex $Cp^*_2Ta(CH_3)(={CH_2})$ to $Cp^*_2Ta(H)(CH_2{=}CH_2)$,[5d] and analogous transformations seen in the C_5H_5 system,[48] the allyl species may reasonably result from a closely analogous vinyl to methylene migration.

Summary

The kinetic stability afforded by two pentamethylcyclopentadienyl ligands on tantalum, combined with the rigorous steric and electronic constraints of the permethyltantalocene fragment, has enabled us to probe in considerable detail some tantalum-mediated hydrocarbon rearrangement processes. In particular, it has proved possible to monitor multiple insertion/elimination steps of types that have not commonly been observed. Some of the key transformations are shown in Scheme VII. β-H elimination from sp^2 carbon plays a pivotal role in the isomerization of allene and butadiene ligands, while α-hydrogen and α-vinyl migratory insertions play a crucial role in the hydrocarbon homologation sequence.

The delineation of the reaction pathway followed in the isomerization of allene and butadiene owes much to the isolation of intermediates whose room-temperature stability would not normally be anticipated. Most notable are the hydrido butadiene and hydrido methylallene derivatives, both apparently favored over the usually thermodynamically preferred π-crotyl ligand arrangement.

The subsequent conversion of the methylallene ligand to propenylidene and then but-2-yne is equally remarkable when compared with related observations for molybdenum[49] and rhodium,[50] both of which have been found to undergo acid-promoted alkyne to allyl rearrangements via allene intermediates, precisely the opposite to our observations for tantalum. The strict 2-fold symmetry for the frontier orbitals of $[Cp^*_2Ta]$ undoubtedly has an important influence on the relative stabilities of these tautomeric species. Their relative stabilities appear to be finely balanced; we have seen that for the C_3 hydrocarbon ligand the metal–allyl bonding mode is favored over the hydrido allene form, yet for C_4 the order is reversed and hydrido methylallene is now preferred to metal crotyl.

A particularly poignant conclusion of these studies is the importance of the hydride ligand in facilitating hydrocarbon rearrangements through reversible migration processes, consistent also with the necessity for a source of added hydrogen (H^+ or H^-) in the alkyne to allyl rearrangements of Green and Werner and the model Fischer–Tropsch studies of Hoel. For the latter, the allene ligand was found to be productive with respect to hydrocarbon chain growth only in the presence of added HBF_4,[13] and our results indicate that a viable pathway exists to metal vinylidenes (and hence to hydrocarbon chain lengthening), provided a metal-bound hydrogen is also present.

Therefore, in considering a mechanism for the role of vinylidenes in the Fischer–Tropsch hydrocarbon-chain-lengthening process, we feel it appropriate to postulate a crucial role for surface-bound hydride. A mechanism for linear hydrocarbon chain growth is shown in Scheme VIII.

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(46) Small amounts of unidentifiable species were also formed.

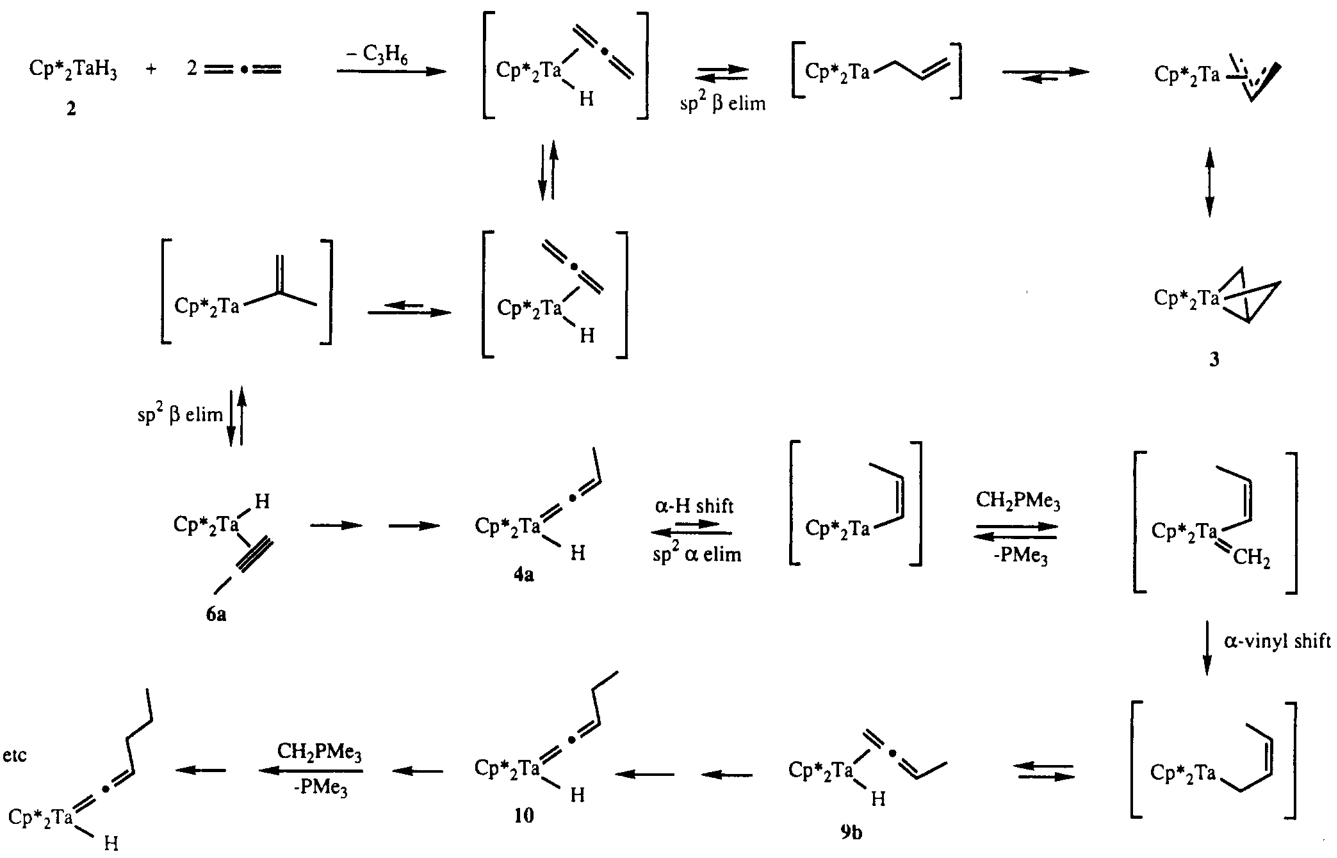
(47) $Cp^*_2Ta(H)(={}^{13}C={}^{13}CH_2)$ was prepared from the reaction of $Cp^*(C_5Me_4(CH_2))TaH_2$ with $H^{13}C{\equiv}^{13}CH$.

(48) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

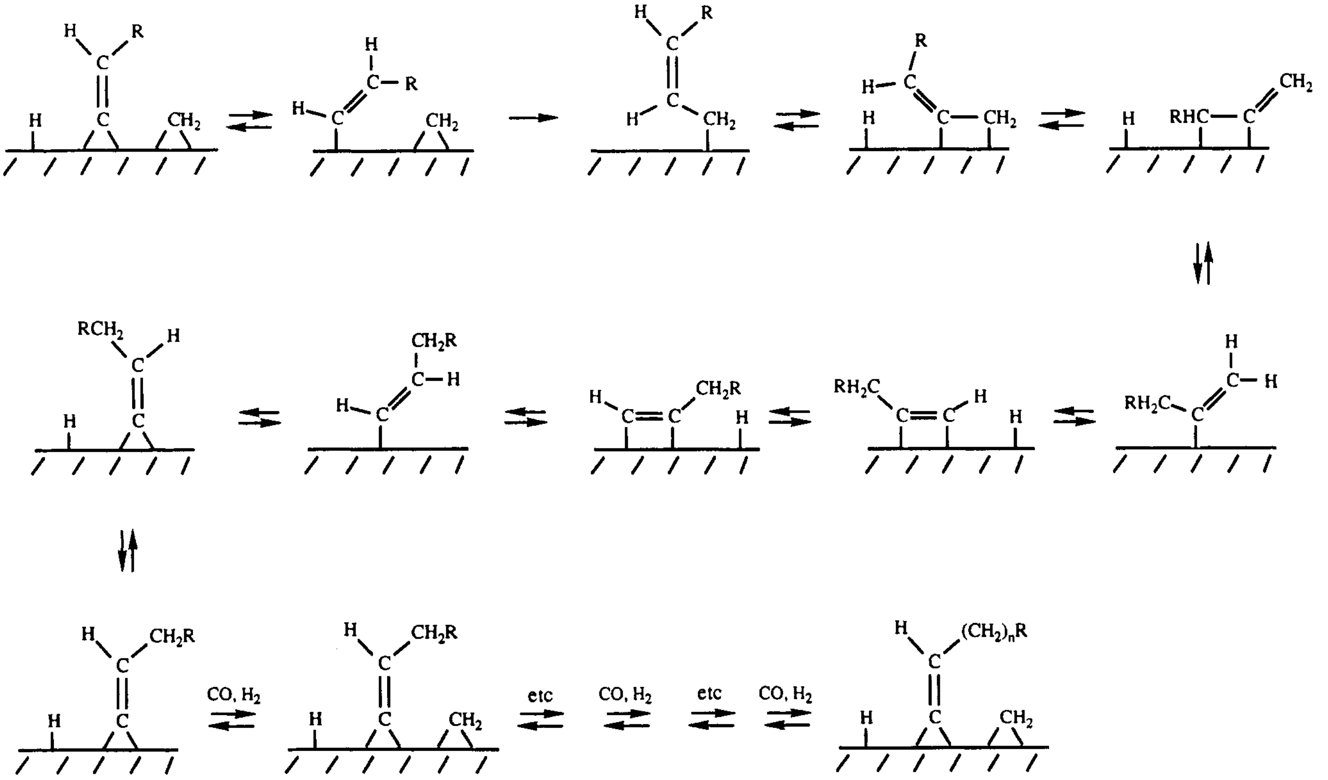
(49) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93 and references therein.

(50) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164.

Scheme VII



Scheme VIII



A key step in this mechanism is the migration of hydride to a vinylidene group to generate a surface alkenyl species, a process closely related to the hydride to methylidene migration proposed by Pettit and co-workers and in contrast to the insertion of methylidene into the vinylidene C=C bond proposed by McCandlish. It is only recently that hydrogen to vinylidene migration has been observed directly,[5c] and comparable insertion rates have been observed for methylidene and vinylidene insertions into the tantalum–hydride bonds of $Cp^*_2TaH(=CH_2)$ and

$Cp^*_2Ta(H)(=C=CH_2)$, respectively.[5d] The subsequent alkenyl to methylene migration is supported by observations on a soluble diiron system[51] and the model studies of Maitlis.[17] It is also in agreement with transient kinetic studies on cobalt, iron, and ruthenium catalysts, which suggest that monomer units add only at the one end of the growing chain.[52]

In summary, the use of bulky ancilliary Cp* ligands on tantalum has allowed a number of complexes possessing very unusual ligand combinations to be observed and isolated during tantalum-mediated rearrangements of some simple conjugated dienes. A modified mechanism for the role of surface vinylidenes in the Fischer–Tropsch hydrocarbon-chain-lengthening process based on reversible hydride migration to vinylidene and subsequent migration of vinyl to surface methylene has emerged from these studies.

Experimental Section

General Considerations. All manipulations were performed on a conventional vacuum line by using standard Schlenk or cannular techniques or in a drybox under an atmosphere of dinitrogen. Solvents were dried and purified by prolonged reflux over $LiAlH_4$ or benzophenone ketyl followed by distillation under an atmosphere of dinitrogen. Ethereal solvents were stored over sodium benzophenone ketyl, and hydrocarbon solvents were stored over titanocene. $Cp^*_2TaCl_2$ and $Cp^*_2TaH_3$ were prepared according to a previously reported procedure.[18] Allene (Matheson), butadiene (Matheson), and allene-d_4 (MSD isotopes) were used as received. 2-Butyne and 2-pentyne were stored over molecular sieves (4A) and distilled prior to use. *trans*-Crotylmagnesium bromide was prepared by a standard Grignard procedure from *trans*-crotyl bromide (Lancaster), while allylmagnesium bromide (Aldrich) and vinylmagnesium bromide (Aldrich) were used as received. Elemental analyses and mass spectral data were provided by the Caltech microanalytical service. Nuclear magnetic resonance spectra were recorded on a Varian EM 390, a Jeol FX90Q, a Bruker WM 500, or a Jeol GX 400Q spectrometer. Infrared spectra were recorded on a Beckman 4240 spectrometer as Nujol mulls and are reported in inverse centimeters. Relative intensities are abbreviated as follows: vs (very strong), s (strong), m (medium), w (weak), bd (broad), sh (shoulder).

Procedures. $Cp^*_2Ta(\eta^3\text{-}C_3H_5)$ (3). Allylmagnesium bromide (1.8 mL of 1.0 M solution; 1.8 mmol) was transferred onto a stirred suspension of $Cp^*_2TaCl_2$ (0.24 g, 0.46 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 48 h to give a deep red solution. The volatile components were removed under reduced pressure, and the residue was dried in vacuo overnight. Extraction with petroleum ether (40 mL) followed by concentration and cooling to −78 °C afforded red microcrystals of **3**. Yield 0.16 g, 70.8%. Anal. Calcd for $C_{23}H_{35}Ta$: C, 56.10; H, 7.11. Found: C, 55.87; H, 7.25. MS: *m/e* 492. IR (cm^{-1}, Nujol): 1720 (w), 1630 (m), 1305 (m), 1020 (s), 940 (m), 885 (m).

$Cp^*_2TaH[=C=CH(CH_3)]$ (4). A thick-walled glass reaction vessel fitted with a Teflon needle valve was charged with $Cp^*_2TaH_3$ (0.5 g, 1.10 mmol), toluene (20 mL), and allene (6.60 mmol) and heated at 80 °C. A ^1H NMR sample was heated under similar conditions and monitored by ^1H NMR spectroscopy. After 5 days, the mixture was transferred to a 110 °C oil bath and heated until conversion to **4** was complete by ^1H NMR spectroscopy (approx 2 days). The volatiles were removed under reduced pressure to give a red residue that was dried overnight in vacuo. Washing with cold petroleum ether (25 mL) gave a white solid that was recrystallized from pentane at −119 °C to afford white crystals of **4**. Yield 0.16 g, 34%. Anal. Calcd for $C_{23}H_{35}Ta$: C, 56.10; H, 7.11. Found: C, 55.88; H, 7.24. MS: *m/e* 492. IR (cm^{-1}, Nujol): 2720 (w), 1775 (m), 1238 (m), 1025 (s), 855 (m), 725 (m).

***endo*-$Cp^*_2TaH(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)$ (8).** Utilizing a similar procedure adopted for **4**, a thick-walled glass reaction vessel fitted with a Teflon needle valve was charged with $Cp^*_2TaH_3$ (0.5 g, 1.10 mmol), toluene (20 mL), and butadiene (3.3 mmol) and heated in a constant temperature oil bath maintained at 50 °C. The reaction was monitored by ^1H NMR spectroscopy on a sample prepared to approximate the conditions. After 21 days, the volatile components were removed under reduced pressure to give a yellow solid that was dried in vacuo overnight. Extraction with petroleum ether (20 mL) gave a yellow solution that on concentration to half volume and cooling to −78 °C, afforded yellow crystals of **8**. Yield 0.4 g, 82.5%. Anal. Calcd for $C_{24}H_{37}Ta$: C, 56.92; H, 7.31. Found: C, 56.52; H, 7.36. MS: *m/e* 506. IR (cm^{-1}, Nujol): 2720 (w), 1800 (m), 1590 (s), 1210 (w), 1145 (w), 1025 (s), 860 (m).

$Cp^*_2TaH(\eta^2\text{-}CH_2{=}C{=}CHCH_3)$ (9). Crotylmagnesium bromide was prepared by addition of crotyl bromide (0.68 g, 5.0 mmol) to magnesium turnings (0.3 g, 12.5 mmol) in THF. The solution was stirred for 2 h at room temperature filtered onto a suspension of $Cp^*_2TaCl_2$ (0.5 g, 1.10 mmol) in THF at −78 °C. The mixture was warmed to room temperature and stirred for 12 h to give a clear orange solution. After removal of the volatile components, the residue was extracted with petroleum ether (80 mL) to give an orange solution, which was filtered, concentrated, and cooled to −78 °C to afford white crystals of **9**. Yield 0.32 g, 66%. Anal. Calcd for $C_{24}H_{37}Ta$: C, 56.92; H, 7.31. Found: C, 56.77; H, 7.38. MS: *m/e* 506. IR (cm^{-1}; Nujol): 2720 (w), 1820 (m), 1765 (m), 1665 (m), 1310 (m), 1293 (m), 1025 (s), 890 (w), 868 (m).

$Cp^*_2TaH[=C=CH(Et)]$ (10). In a similar manner described for **4** and **8**, a thick-walled glass reaction vessel was charged with $Cp^*_2TaH_3$ (0.5 g, 1.10 mmol), toluene (20 mL), and butadiene (6.6 mmol). The mixture was stirred at 80 °C for 5 days and then transferred to a 110 °C oil bath until conversion to **10** was optimized by ^1H NMR spectroscopy (approx 6 h at 110 °C). A yellow solution resulted. After removal of the volatile components under reduced pressure, the residue was dried overnight in vacuo and extracted with petroleum ether (50 mL). The resulting yellow solution was filtered, concentrated, and cooled to −78 °C to give white crystals of **10**. Yield 0.35 g, 72%. Anal. Calcd for $C_{24}H_{37}Ta$: C, 56.92; H, 7.31. Found: C, 56.77: H, 7.27. MS: *m/e* 506. IR (cm^{-1}, Nujol): 2720 (w), 1795 (s), 1735 (m), 1260 (m), 1225 (m), 1025 (s), 880 (w), 860 (w), 800 (w), 775 (m).

$Cp^*_2Ta(H)(MeC{\equiv}CMe)$ (11). A thick-walled glass reaction vessel fitted with a Teflon needle valve was charged with $Cp^*_2TaH_3$ (0.5 g, 1.10 mmol), toluene (20 mL), and but-2-yne (2.20 mmol) and heated at 110 °C with stirring for 5 days to give a pale yellow solution. The volatile components were removed under reduced pressure to give a yellow solid that was dried in vacuo. Recrystallization from pentane (15 mL) at −78 °C afforded white crystals of 11. Yield 0.49 g, 88%. Anal. Calcd for $C_{24}H_{37}Ta$: C, 56.92; H, 7.31. Found: C, 56.93; H, 7.32. MS: *m/e* 506. IR (cm^{-1}, Nujol): 2720 (w), 1790 (m), 1750 (m).

Reaction of $Cp^*(C_5Me_4(CH_2))TaH_2$ with $CH_3C{\equiv}CH$. A solution of $Cp^*(C_5Me_4(CH_2))TaH_2$ (20 mg) in C_6D_6 (0.7 mL) was treated with excess $CH_3C{\equiv}CH$ in a NMR tube and sealed at −196 °C. The tube was allowed to warm to room temperature and then heated at 80 °C for 1 h. The formation of **6b** was established by ^1H NMR.

Reaction of $Cp^*_2Ta(H)(=C=CH_2)$ with CH_2PMe_3. A solution of $Cp^*_2Ta(H)(=C=CH_2)$ (ca. 50 mg) in C_6D_6 (0.7 mL) was treated with a 3-fold excess of CH_2PMe_3 in a sealed NMR tube. The mixture was heated at 110 °C for 2 days, and the products were analyzed by ^1H NMR spectroscopy.

Reaction of $Cp^*_2Ta(H)(={}^{13}C={}^{13}CH_2)$ with CH_2PMe_3. A solution of $Cp^*_2Ta(H)(={}^{13}C={}^{13}CH_2)$ (ca. 50 mg) in C_6D_6 (0.7 mL) was treated with excess CH_2PMe_3 and heated under similar conditions to the unlabeled mixture. The products were analyzed by ^{13}C NMR spectroscopy.

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(52) (a) Mims, C. A.; McCandlish, L. E. *J. Phys. Chem.* **1987**, *91*, 929. (b) Mims, C. A.; McCandlish, L. E.; Melchior, M. T. *Catal. Lett.* **1988**, *1*, 121.

Organometallics **1991**, *10*, 231–238

Science and Engineering Research Council, U.K.

Registry No. **3**, 130031-79-7; **4a**, 130031-80-0; **4b**, 130143-25-8; **6a**, 130143-23-6; **6b**, 130031-78-6; **7**, 130031-84-4; 8, 130031-81-1; **9a**, 130031-82-2; **9b**, 130143-24-7; **10**, 130031-83-3; 11, 100701-98-2; $Cp^*_2TaH_3$, 100701-94-8; C_3H_5MgBr, 1730-25-2; *trans*-$CH_3CH{=}CHCH_2MgBr$, 36306-56-6; $Cp^*_2TaCl_2$, 100701-93-7; $CH_2{=}C{=}CH_2$, 463-49-0; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $CH_3C{\equiv}CCH_3$, 503-17-3; $CH_3C{\equiv}CH$, 74-99-7; $Cp^*_2Ta(H)({=}C{=}CH_2)$, 103619-53-0; $CH_2{=}PMe_3$, 14580-91-7.

Preparation of Tricarbonyl(η^4-vinylketene)iron(0) Complexes from Tricarbonyl(η^4-vinyl ketone)iron(0) Complexes and Their Subsequent Conversion to Tricarbonyl(η^4-vinylketenimine)iron(0) Complexes

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Reaction of tricarbonyl(η^4-vinyl ketone)iron(0) complexes $(CO)_3(PhCH{=}CHC(R){=}O)Fe(0)$ (R = Me, **1**; Bu^n, **3**; Bu^t, **5**; Ph, **7**) with organolithium reagents under an atmosphere of carbon monoxide gave products that were identified as tricarbonyl"(η^4-vinylketene)"iron(0) complexes $(CO)_3(PhCH{=}CHC(R){=}C{=}O)Fe(0)$ (R = Me, **2**; Bu^n, **4**; Bu^t, **6**; Ph, **8**) based on a crystal structure analysis of **2**. Complex **2** crystallizes in space group $P2_1/c$ with $a = 13.998\ (6)$ Å, $b = 7.955\ (5)$ Å, $c = 12.935\ (5)$ Å, $\beta = 113.04\ (3)°$, and $Z = 4$. A reaction pathway that postulates the intermediacy of a tricarbonyl(η^3-vinylcarbene)iron(0) complex, **20**, is discussed. Heating the tricarbonyl(η^4-vinylketene)iron(0) complexes **6** and **2** with either *tert*-butyl, cyclohexyl, or 2,6-xylyl isocyanide at 80 °C gave tricarbonyl"(η^4-vinylketenimine)"iron(0) complexes $(CO)_3(PhCH{=}CHC(R^1){=}C{=}NR^2)Fe(0)$ ($R^1 = R^2 =$ Bu^t, **23**; R^1 = Me, R^2 = Bu^t, **24**; R^1 = Me, $R^2 = C_6H_{11}$, **25**; R^1 = Me, $R^2 = (2,6\text{-}Me_2)C_6H_3$, **26**) via intermediate dicarbonyl(isocyanide)(η^4-vinylketene)iron(0) complexes. The intermediacy of tricarbonyl(isocyanide)(η^1-vinylcarbene)iron(0) complexes in this reaction is proposed.

Introduction

Investigations into the reactivity of vinyl ketones complexed to the tricarbonyliron(0) moiety have been neglected in the past in favor of investigations into the reactivity of 1,3-dienes complexed to the tricarbonyliron(0) unit.[1] This is somewhat surprising in view of the central role played by carbonyl compounds in organic synthesis and the potential that these complexes hold for exerting high stereochemical control over reactions of the vinyl ketone ligand. The major application of tricarbonyl(η^4-vinyl ketone)iron(0) complexes to date has been their use as a source of the tricarbonyliron(0) unit, which may be transferred from the vinyl ketone ligand to 1,3-dienes under relatively mild conditions.[2] Other investigations have revealed that they may be protonated[3] or acylated[4] on the ligand oxygen atom and that on heating they cyclodimerize to generate cyclopentene derivatives.[5]

Some time ago we reported the first examples of nucleophilic attack on tricarbonyl(η^4-vinyl ketone)iron(0) complexes.[6] We demonstrated that reactions of Grignard and organolithium reagents with a range of complexes under a nitrogen atmosphere produced 1,4-diketones in good yield, presumably via nucleophilic attack on a metal carbonyl ligand. This chemistry has been subsequently applied to the synthesis of dihydrojasmone and the formal synthesis of cuparene.[7] Recently it has been reported that addition of $LiCMe_2CN$ to an iron(0) complex of a vinyl ketone resulted in a Michael-type addition; i.e., direct attack on the organic ligand occurred.[8] This observation is consistent with the results obtained from studies on tricarbonyl(η^4-1,3-diene)iron(0),[9] tetracarbonyl(η^2-vinyl ester)iron(0),[10] and tetracarbonyl(η^2-vinylamide)iron(0)[11] complexes, which show that in these systems alkyllithium and Grignard reagents add to a carbonyl ligand while

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