Organometallics **1984**, *3*, 159-163

Conclusions

It is clear that hydrogen bridge formation is more important in $(Cp_2NbH_2)_2Zn$ than in Cp_2NbH_2ZnCp. In the former compound, the zinc atom is coordinatively unsaturated and tries to relieve this unsaturation by the formation of hydrogen bridges. In the latter compound, however, the zinc atom is already coordinatively saturated through η^5-coordination of the Cp(Zn) group, and hydrogen bridge formation is unnecessary.

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Registry No. $(Cp_2NbH_2)_2Zn$, 39430-61-0; $Cp_2NbH(ZnCp)_2$, 87432-58-4; Cp_2NbH_2ZnCp, 87432-59-5; Cp_2NbH_3, 11105-67-2; Cp_2Zn, 11077-31-9.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Tantalum–Zinc Compounds—Structure of $(CH_3C_5H_4)_2TaH(ZnC_5H_5)_2$

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From the reaction of $Cp'TaH_3$ ($Cp' = CH_3C_5H_4$) with Cp_2Zn, four different compounds containing tantalum–zinc bonds have been isolated: $(Cp'_2TaH_2)_2Zn$, Cp'_2TaH_2ZnCp, and two isomers of $Cp'_2TaH(ZnCp)_2$. The crystal structure of the most stable of the two isomers was determined by a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions $a = 15.519$ (3) Å, $b = 8.461$ (4) Å, $c = 15.52$ (1) Å, and $\beta = 99.99$ (4)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R_F = 0.036$ ($R_{wF} = 0.041$) for 1845 observed reflections and 293 parameters. The molecule resembles that of Cp_2TaH_3, with two adjacent hydrogen atoms replaced by ZnCp groups. The geometry of the Cp'_2Ta fragment is normal, with the methyl groups located approximately above and below the tantalum-bound hydride. The Cp(Zn) rings are bound in a somewhat asymmetrical η^5 fashion. On the basis of NMR evidence, a similar structure with the remaining hydride now occupying a central position is assigned to the less stable isomer of $Cp'_2TaH(ZnCp)_2$. The reaction of $Cp_2Ta(olefin)H$ with Cp_2Zn proceeds with loss of olefin to give $Cp_2Ta(ZnCp)_3$ as the final product. According to NMR data, this compound has a structure analogous to that of Cp_2TaH_3, with all three hydrides replaced by ZnCp groups.

Introduction

In the preceding paper[1] we reported the synthesis and characterization of the two new niobium–zinc compounds, obtained from the reaction of Cp_2NbH_3 with Cp_2Zn. Attempts to extend these reactions to derivatives of other niobium hydrides were, however, hampered by the reactivity of these niobium compounds and their zinc derivatives. Therefore, we extended our investigations in transition-metal–zinc compounds[1-3] to the heavier group 5B metal tantalum. Several mixed-metal tantalum compounds are known: $Cp_2TaH_2SnMe_3$,[4] $\{[Cp_2Ta(\mu\text{-}SMe)_2]_2Pt\}Cl_2$,[5,6] and some salt-like derivatives of the hexacarbonyltantalate anion.[7,8]

No tantalum–zinc compounds have been reported up to now. Although Cp_2NbH_3 reacted with Et_2Zn to form $(Cp_2NbH_2)_2Zn$, reaction of Cp_2TaH_3 with Et_2Zn resulted only in formation of a loose adduct.[9] We have found that Cp_2Zn is generally more reactive toward transition-metal hydrides than dialkyl- and diarylzinc compounds.[1,2] Therefore, we decided to investigate the reactions of Cp'_2TaH_3 ($Cp' = CH_3C_5H_5$) and $Cp_2Ta(olefin)H$ with Cp_2Zn.

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were

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Table I. Crystal Data and Details of the Structure Determination

(a) Crystal Data	
formula	$C_{22}H_{25}Zn_2Ta$
mol wt	601.13
cryst system	monoclinic—*b*
space group	No. 14, $P2_1/n$
a, Å	15.519 (3)
b, Å	8.461 (4)
c, Å	15.52 (1)
β, deg	99.99 (4)
V, Å^3	2007 (2)
Z	4
D_{calcd}, g/cm^{-1}	1.989
$F(000)$	1160
μ(Mo Kα), cm^{-1}	81.52
cryst size, mm	$(001)\rightarrow(00\bar{1})$, 0.375 $(010)\rightarrow(0\bar{1}0)$, 0.25 $(100)\rightarrow(\bar{1}00)$, 0.125
cryst vol, mm^3	0.012
no. of grid points for abs cor	560
min and max transmission	0.125, 0.381
(b) Data Collection	
θ_{min}, θ_{max}, deg	0.1, 22.0
radiation	Mo Kα, Zr filtered, 0.710 69 Å
$\omega/2\theta$ scan, deg	0.50 + 0.35 tan θ
max time/reflctn, min	1
horizontal and vertical aperture, mm	3, 6
ref reflctns	200, $\bar{2}00$
total data	2450
total unique	2119
obsd data ($I > 2.5\sigma(I)$)	1845
total X-ray exp time, h	39.1
(c) Refinement	
no. of refined parameters	293
wtg scheme	$w^{-1} = (\sigma^2(F) + 0.0044F^2)/0.74$
final $R_F = \Sigma \lvert F_o - \lvert F_c\rvert\rvert / \Sigma F_o$	0.036
final $R_{wF} = [\Sigma w(F_o - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$	0.041
rms dev of rflctn of unit wt	2.91

recorded on Varian EM-390 and CFT-20 and Bruker WP-200 spectrometers. Cp_2Zn[10] and $Cp_2Ta(C_3H_6)H$[11] were prepared by literature methods, and $Cp_2Ta(C_2H_4)H$ was prepared similar to $Cp_2Ta(C_3H_6)H$. Cp'_2TaH_3 was prepared by a procedure analogous to the one described for Cp_2NbH_3.[12]

$(Cp'_2TaH_2)_2Zn$. To a suspension of 0.12 g (0.6 mmol) of Cp_2Zn in 5 mL of benzene was added a solution of 0.44 g (1.3 mmol) of Cp'_2TaH_3 in 15 mL of benzene, and the solution was refluxed for 4 h. An ^{1}H NMR spectrum after this period showed no absorptions due to Cp'_2TaH_2ZnCp. The benzene was removed in vacuo, and the residue was dissolved in 25 mL of pentane. The solution was concentrated in vacuo and cooled to −60 °C to yield orange-red crystals of $(Cp'_2TaH_2)_2Zn$.

Cp'_2TaH_2ZnCp. A solution of 0.56 g (1.6 mmol) of Cp'_2TaH_3 in 15 mL of benzene was added to a suspension of 0.3 g (1.5 mmol) of Cp_2Zn in 5 mL of benzene. The solution was stirred for 1 h at room temperature, and the solvent was removed in vacuo. The pale yellow product was washed twice with 5 mL of pentane and dried in vacuo; yield 0.38 g (53%). Anal. Found (Calcd): C 43.95 (43.29); H, 4.10 (4.49); Zn, 13.67 (13.86).

$Cp'_2TaH(ZnCp)_2$ (Isomer I). To a suspension of 3.54 g (18.1 mmol) of Cp_2Zn in 20 mL of benzene was added a solution of 1.54 g (4.5 mmol) of Cp'_2TaH_3 in 40 mL of benzene. The mixture was refluxed for 3 h, and after the mixture was cooled to room temperature, the excess of Cp_2Zn was removed by centrifugation. The solvent was removed in vacuo, and the product was washed with 20 mL of pentane; yield 1.21 g (45%). Yellow crystals, suitable for X-ray diffraction analysis, were obtained by crystallization from diethyl ether (30 °C/−50 °C); mol wt 600 ± 10 (calcd 601), by ebulliometry in benzene.

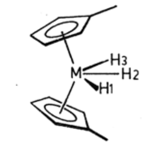


Figure 1. The adopted numbering of the hydrides in Cp'_2MH_3 molecules.

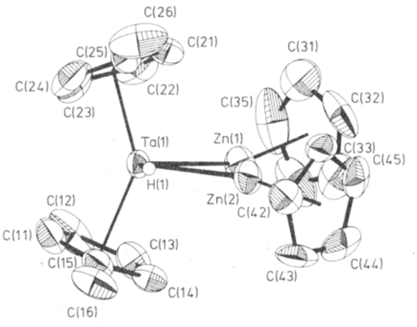
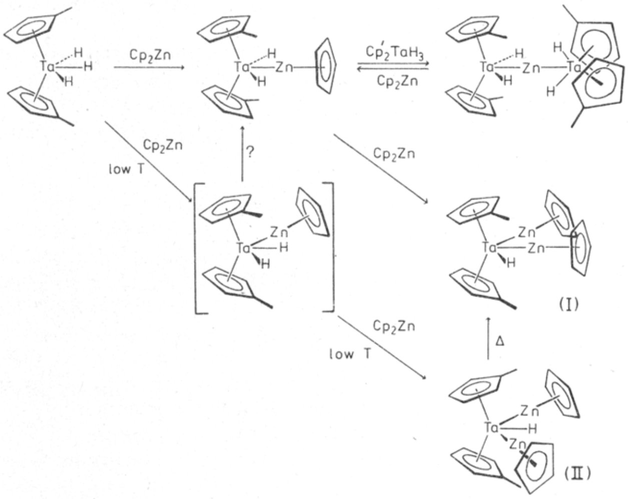


Figure 2. ORTEP drawing of $Cp'_2TaH(ZnCp)_2$ (I), showing 40% probability thermal ellipsoids. All hydrogen atoms except H(1) have been omitted for clarity.

Scheme I



$Cp'_2TaH(ZnCp)_2$ (Isomer II). A cooled solution of 0.89 g (2.6 mmol) of Cp'_2TaH_3 in 15 mL of toluene was added to a stirred suspension of 2.15 g (11.0 mmol) of Cp_2Zn in 20 mL of toluene at −70 °C. The stirred reaction mixture was warmed in the course of 3 h to room temperature. The excess of Cp_2Zn was removed by centrifugation, and the solvent was removed in vacuo. The off-white product was washed four times with 20 mL of pentane and dried in vacuo; yield 0.52 g (33%).

$Cp_2Ta(ZnCp)_3$. A mixture of 0.54 g (1.5 mmol) of $Cp_2Ta(C_3H_6)H$ and 1.04 g (5.2 mmol) of Cp_2Zn in 35 mL of benzene was stirred under reflux for 5 h. The solvent was removed in vacuo, and the residue was extracted 30 mL of diethyl ether. The product, an orange-brown powder, was obtained by cooling the ethereal solution to −60 °C. Anal. Found (Calcd): C, 41.57 (42.74); H, 3.92 (3.59); Zn, 27.92 (27.92). The same product was obtained from $Cp_2Ta(C_2H_4)H$.

Data Collection and Structure Determination of $Cp'_2TaH(ZnCp)_2$ (Isomer I). A yellow crystal suitable for data collection was sealed under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD4F diffractometer. Several ω scan reflection profiles indicated that the crystal con-

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Table II. ^1H and ^{13}C NMR Data for Tantalum-Zinc Compounds[a]

		Cp(Ta) or Cp′(Ta)		
^1H NMR	Cp(Zn)	H(ring)	H(Me)	H(Tm)
$(Cp'_2TaH_2)_2Zn$		4.58	2.14	−8.24
Cp'_2TaH_2ZnCp	6.63	4.41	1.97	−6.80
$Cp'_2TaH(ZnCp)_2$ (I)	6.30	3.66, 3.86, 4.29, 4.65[d]	1.81	−9.00
$Cp'_2TaH(ZnCp)_2$ (II)	6.56	4.38	1.89	−7.35
$Cp_2Ta(ZnCp)_3$	6.50[d]	3.85		
Cp'_2TaH_3		4.70, 4.83[b]	1.98	−1.69, −3.20
Cp_2TaH_3		4.86		−1.63, −3.02
Cp_2Zn	6.33			

		Cp(Ta) or Cp′(Ta)	
^{13}C NMR	Cp(Zn)	C(ring)	C(Me)
$Cp'_2TaH(ZnCp)_2$ (I)	106.0	70.5, 72.6, 77.7, 79.5	16.0
$Cp_2Ta(ZnCp)_3$	107.2, 106.4	70.4	
Cp_2Zn	114.4		

[a] C_6D_6, δ in ppm relative to internal Me_4Si. [b] AA′BB′ pattern. [c] AA′BB′ pattern with $\delta_A \approx \delta_B$. [d] At 30 °C; values are temperature dependent probably due to hindered rotation of the Cp′(Ta) groups. [e] In toluene at −70 °C: 6.68 and 6.71 ppm (2:1). [f] The absorption due to C_1 could not be identified in the 200-MHz spectrum. It may coincide with one of the other Cp′(Ta) carbon atoms. [g] Intensity ratio 1:2.

sisted of two fragments, whose relative orientation could be described by small rotation about a vector $\vec{A}$. This model was used to calculate ψ values at which the profile of a reflection to be scanned appeared as unsplit (the A model[13]). Unit cell dimensions and standard deviations were determined in the usual way from the setting angles of 13 carefully centered reflections.[14] The intensities of one quadrant of the reflection sphere ($\pm h,+k,+l$) were collected in the $\omega/2\theta$ scan mode, with use of Zr-filtered Mo Kα radiation. The intensities of two reference reflections were monitored every hour of X-ray exposure time. There was no indication for decay during the data collection; the fluctuations in the control reflections were less than 3%. The data were corrected for absorption and for Lorentz and polarization effects in the previously described way.[14] Details of the data collection and structure determination are summarized in Table I. The structure was solved by standard Patterson and Fourier methods and subsequently refined by (blocked) full-matrix least-squares techniques. Positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. The methyl groups of the Cp′(Ta) rings were refined as rigid groups, with one overall variable isotropic thermal parameter for the six hydrogen atoms and three rotational parameters per methyl group. The Cp′(Ta) and Cp(Zn) ring hydrogen atoms were initially placed at calculated positions and subsequently refined satisfactorily; they were divided in two groups (those of the Cp′(Ta) and those of the Cp(Zn) rings), each of which was assigned one overall variable isotropic thermal parameter. The tantalum-bound hydride was located from a difference Fourier. Although it was not the highest peak in the difference Fourier, it was the only one which was located at a chemically reasonable distance from Ta and the only one which was refined satisfactorily. The assignment was supported by the observation that its relative height in the difference Fourier increased sharply (with respect to the "ghost peaks" around Ta) when the data set was truncated at low $(\sin\theta)/\lambda$ values.[15] The "ghost peaks" around Ta were probably caused by imperfect absorption correction. Weights were introduced in the final refinement stages. The refinement converged at $R_F = 0.036$ ($R_{wF} = 0.041$) for 293 parameters, 1845 reflections, and $w^{-1} = (\sigma^2(F) + 0.044F^2)/0.74$. Neutral atom scattering factors were taken from ref 16 and corrected for anomalous dispersion.[17] All calculations were carried out on the Cyber 175 of the University of Utrecht Computer Center. Programs used include: SHELX-76 (structure determination and refinement[18]), PLATO (geometry analysis[19]), and ORTEP (plotting program[20]).

Table III. Fractional Atomic Coordinates for $Cp'_2TaH(ZnCp)_2$ (Cp and Cp′ Hydrogen Atoms Excluded)

	x/a	y/b	z/c
Ta(1)	0.22546 (3)	0.16255 (5)	−0.05987 (3)
Zn(1)	0.1835 (1)	0.3441 (2)	0.0606 (1)
Zn(2)	0.3477 (1)	0.2311 (2)	0.07077 (9)
C(11)	0.2313 (9)	0.206 (2)	−0.2092 (8)
C(12)	0.1603 (9)	0.295 (3)	−0.1867 (9)
C(13)	0.1973 (9)	0.414 (2)	−0.1265 (8)
C(14)	0.2882 (8)	0.392 (1)	−0.1121 (7)
C(15)	0.3071 (8)	0.266 (2)	−0.1653 (7)
C(16)	0.399 (1)	0.220 (2)	−0.1755 (9)
C(21)	0.183 (1)	−0.027 (2)	0.0409 (8)
C(22)	0.108 (1)	0.039 (2)	−0.011 (1)
C(23)	0.112 (1)	−0.015 (2)	−0.094 (1)
C(24)	0.186 (1)	−0.101 (2)	−0.093 (1)
C(25)	0.231 (1)	−0.112 (2)	−0.0100 (9)
C(26)	0.310 (1)	−0.211 (2)	0.020 (1)
C(31)	0.095 (1)	0.313 (2)	0.180 (1)
C(32)	0.172 (1)	0.378 (2)	0.2104 (9)
C(33)	0.178 (1)	0.516 (3)	0.169 (1)
C(34)	0.105 (2)	0.540 (2)	0.113 (1)
C(35)	0.051 (1)	0.414 (4)	0.118 (1)
C(41)	0.4520 (9)	0.165 (2)	0.1830 (8)
C(42)	0.4996 (8)	0.186 (2)	0.1129 (9)
C(43)	0.497 (1)	0.345 (2)	0.090 (1)
C(44)	0.4523 (9)	0.420 (2)	0.148 (1)
C(45)	0.4236 (9)	0.310 (2)	0.2048 (9)
H(1)	0.318 (6)	0.100 (9)	−0.045 (5)

Results and Discussion

Reaction of Cp'_2TaH_3 with Cp_2Zn. From the reaction of Cp'_2TaH_3 with Cp_2Zn (1:1) in benzene, the compound Cp'_2TaH_2ZnCp could be obtained pure. Prolonged heating with an excess of Cp'_2TaH_3 was required to convert this into $(Cp'_2TaH_2)_2Zn$. In view of the lower reactivity of Et_2Zn toward metal hydrides, the failure of this compound to react with Cp_2TaH_3[9] is not surprising in retrospect. The ^1H NMR spectra of both tantalum–zinc compounds show an AA′BB′ pattern for the ring protons of the Cp′(Ta) ring, which implies that these species have been formed from the trihydride by substitution of the central hydrogen atom (H(2)) (Figure 1).

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Table IV. Selected Bond Distances (Å)

Ta(1)-Zn(1)	2.588 (2)	Zn(1)-Zn(2)	2.700 (2)	C(11)-C(12)	1.43 (2)	C(31)-C(32)	1.32 (3)
Ta(1)-Zn(2)	2.590 (2)	Zn(2)-H(1)	2.09 (8)	C(12)-C(13)	1.43 (2)	C(32)-C(33)	1.34 (3)
Ta(1)-H(1)	1.52 (9)	Zn(1)-C(31)	2.50 (2)	C(13)-C(14)	1.40 (2)	C(33)-C(34)	1.32 (4)
Ta(1)-C(11)	2.36 (1)	Zn(1)-C(32)	2.38 (1)	C(14)-C(15)	1.41 (2)	C(34)-C(35)	1.37 (4)
Ta(1)-C(12)	2.34 (2)	Zn(1)-C(33)	2.24 (2)	C(15)-C(11)	1.35 (2)	C(35)-C(31)	1.37 (3)
Ta(1)-C(13)	2.37 (2)	Zn(1)-C(34)	2.28 (2)	C(15)-C(16)	1.51 (2)	C(41)-C(42)	1.43 (2)
Ta(1)-C(14)	2.37 (1)	Zn(1)-C(35)	2.45 (2)	C(21)-C(22)	1.42 (2)	C(42)-C(43)	1.39 (2)
Ta(1)-C(15)	2.40 (1)	Zn(2)-C(41)	2.23 (1)	C(22)-C(23)	1.38 (3)	C(43)-C(44)	1.38 (2)
Ta(1)-C(21)	2.41 (1)	Zn(2)-C(42)	2.37 (1)	C(23)-C(24)	1.37 (2)	C(44)-C(45)	1.41 (2)
Ta(1)-C(22)	2.35 (2)	Zn(2)-C(43)	2.48 (2)	C(24)-C(25)	1.36 (2)	C(45)-C(41)	1.37 (2)
Ta(1)-C(23)	2.30 (2)	Zn(2)-C(44)	2.44 (2)	C(25)-C(21)	1.38 (2)		
Ta(1)-C(24)	2.35 (1)	Zn(2)-C(45)	2.31 (1)	C(25)-C(26)	1.48 (2)		
Ta(1)-C(25)	2.45 (1)						

Table V. Selected Bond Angles (deg)

Zn(1)-Ta(1)-Zn(2)	62.8 (1)	C(43)-C(44)-C(45)	111 (1)	C(14)-C(15)-C(16)	124 (1)
Zn(2)-Ta(1)-H(1)	54 (3)	C(44)-C(45)-C(41)	107 (1)	C(21)-C(22)-C(23)	103 (1)
C(31)-C(32)-C(33)	109 (2)	C(45)-C(41)-C(42)	108 (1)	C(22)-C(23)-C(24)	110 (2)
C(32)-C(33)-C(34)	109 (2)	C(11)-C(12)-C(13)	107 (1)	C(23)-C(24)-C(25)	110 (2)
C(33)-C(34)-C(35)	107 (2)	C(12)-C(13)-C(14)	107 (1)	C(24)-C(25)-C(21)	106 (1)
C(34)-C(35)-C(31)	107 (2)	C(13)-C(14)-C(15)	108 (1)	C(25)-C(21)-C(22)	111 (1)
C(35)-C(31)-C(32)	108 (2)	C(14)-C(15)-C(11)	109 (1)	C(21)-C(25)-C(26)	128 (1)
C(41)-C(42)-C(43)	109 (1)	C(15)-C(11)-C(12)	109 (1)	C(24)-C(25)-C(26)	126 (1)
C(42)-C(43)-C(44)	106 (1)	C(11)-C(15)-C(16)	127 (1)		

From Cp'_2TaH_3 and excess Cp_2Zn at room temperature or above, a compound $Cp'_2TaH(ZnCp)_2$ (I) is obtained. The ^1H NMR spectrum of this compound shows four distinct multiplets for the Cp′(Ta) ring protons, indicating that the substitution at Ta is not symmetrical (i.e., substitution of H(1) and H(2)). This substitution pattern was confirmed by an X-ray diffraction study (vida infra). If, however, the reaction between Cp'_2TaH_3 and excess Cp_2Zn was carried out by mixing the reagents at −70 °C and letting them warm up to 20 °C, an isomeric compound, $Cp'_2TaH(ZnCp)_2$ (II), was obtained. The ^1H NMR spectrum of this isomer exhibited an AA′BB′ pattern for the Cp′(Ta) ring protons, indicating symmetrical substitution at Ta (i.e., substitution of H(1) and H(3)). Isomer II is converted irreversibly and completely into I when heated in benzene solution at 50 °C for 3 h. No equilibrium between these species was observed. The formation of the 1,3-substituted isomer can only be explained by assuming that at low temperature Cp_2Zn preferentially attacks one of the outer hydrogen atoms of Cp'_2TaH_3. It may be that the methyl groups of the Cp′ rings, which in their most stable conformation point to positions directly above and below the central hydride position, hinder the approach of Cp_2Zn toward this hydrogen atom. At higher temperatures, the increasingly free rotation of the Cp′ rings will diminish the effect of this steric hindrance. Also, isomerization of the intermediate 1-Cp'_2TaH_2ZnCp to Cp'_2TaH_2ZnCp, a process similar to the isomerization of II into I, may occur at higher temperatures. The (partly hypothetical) reaction scheme is presented in Scheme I.

Crystal Structure of $Cp'_2TaH(ZnCp)_2$ (I). An ORTEP drawing of the title compound, along with the adopted numbering scheme, is shown in Figure 2. Atomic coordinates are given in Table III, selected bond distances in Table IV, and bond angles in Table V. The arrangement of ligands around the Ta atom resembles that found in Cp_2TaH_3.[21] The methyl groups of the Cp′(Ta) rings are positioned above and below the tantalum-bound hydride, and the Cp'_2TaHZn_2 unit has an approximate mirror plane passing through the metal atoms. The Cp'_2Ta fragment has a normal geometry, with a bending angle of 137.5 (9)° and average Ta–C and C–C distances of 2.37 (1) and 1.39 (1) Å. The ZnTaZn angle of 62.8 (1)° is equal to the inner HTaH angles in Cp_2TaH_3 (62.8 (5) and 63.0 (4)°[21]), which emphasizes the narrow range of geometrical variation that is possible within the ML_3 fragment of a Cp_2ML_3 complex. The small ZnTaZn angle results in a very close approach of the two nonbonded zinc atoms (2.699 (2) Å; Cf. 2.69 Å in zinc metal). The HTaZn angle (54 (3)°) is close to the HNbZn angle of 51 (1)° in Cp_2NbH_2ZnCp.[1] The two Ta–Zn distances are equal within experimental error, indicating that both bonds are normal single bonds and that the hydrogen atom does not bridge between Ta and Zn(2). The Cp(Zn) rings are bound to the zinc atoms in a η^5 fashion, with perpendicular zinc–ring distances of 2.06 (6) and 2.03 (4) Å; the bonding, however, deviates considerably from its ideal symmetry. When M_{Cp} denotes the center of gravity of the Cp ring, the $TaZnM_{Cp}$ angles are 161.4 (4) and 164.2 (4)°, and the angles between Zn–M_{Cp} and the Cp planes are 82.2 (4) and 83.0 (4)°. Both the bond distances and the deformations resemble those found in $(CpZn)_2Co(Cp)PPh_3$[2] and are ascribed to the repulsion between the two Cp(Zn) rings that are forced together very closely in this molecule. In $Cp_2NbZnCp$, in which no significant crowding occurs, the bonding of the Cp(Zn) groups is nearly symmetrical.[1]

Reaction of $Cp_2Ta(olefin)H$ with Cp_2Zn. As noted above, we have not been able to prepare $Cp'_2Ta(ZnCp)_3$ from Cp'_2TaH_3 and excess Cp_2Zn; nor was it possible to obtain $Cp_2Nb(ZnCp)_3$ from Cp_2NbH_3 and Cp_2Zn.[1] We were, therefore, surprised to find that $Cp_2Ta(ZnCp)_3$ was formed in the reaction between $Cp_2Ta(olefin)H$ (olefin = C_2H_4, C_3H_6) and Cp_2Zn. The reaction between $Cp_2Ta(propene)H$ and Cp_2Zn was followed by ^1H NMR spectroscopy. The starting material consisted of a 40/60 mixture of the endo and exo isomers;[11] in both isomers, the Cp(Ta) rings are inequivalent and are observed separately in the NMR spectrum. The initial reaction product, which was formed slowly at room temperature, was again a mixture of two compounds in the approximate ratio of 40/60, each of which contained one Cp(Zn) ring and two inequivalent Cp(Ta) rings (the rest of the spectrum was complicated and could not be interpreted). These observations would be in accord with the initial formation of the expected product $Cp_2Ta(propene)ZnCp$. The same mixture was, however, obtained from $Cp_2Ta(ethene)H$, which does not have endo and exo isomers. Therefore, it

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seems likely that the intermediate is a mixture of the endo and exo isomers of Cp_2Ta(cyclopentadiene)ZnCp. The initial product could not be obtained pure because of the occurrence of a subsequent reaction, which was slow at room temperature and resulted in formation of the final product $Cp_2Ta(ZnCp)_3$. This compound was characterized by ^1H and ^{13}C NMR spectroscopy (Table II) and elemental analysis. Hydrolysis gave the expected products Cp_2TaH_3, $Zn(OH)_2$, and cyclopentadiene. The mechanism of the formation of $Cp_2Ta(ZnCp)_3$ is still unclear.

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Registry No. $(Cp'_2TaH_2)_2Zn$, 87451-31-8; Cp'_2TaH_2ZnCp, 87451-32-9; $Cp'_2TaH(ZnCp)_2$ (isomer I), 87451-33-0; $Cp'_2TaH(ZnCp)_2$ (isomer II), 87507-30-0; Cp_2Zn, 11077-31-9; Cp'_2TaH_3, 41370-94-9; $Cp_2Ta(ZnCp)_3$, 87451-34-1; $Cp_2Ta(C_3H_6)H$ (endo isomer), 68586-68-5; $Cp_2Ta(C_3H_6)H$ (exo isomer), 68680-01-3; $Cp_2Ta(C_2H_4)H$, 66786-38-7; Zn, 7440-66-6; Ta, 7440-25-7.

Supplementary Material Available: Listings of structure factor amplitudes, all positional and thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

Optically Active Transition-Metal Compounds. 80.[1] Synthesis, Stereochemistry, and X-ray Analysis of Allylcarbonylnitrosyl(aminophosphine)iron Complexes

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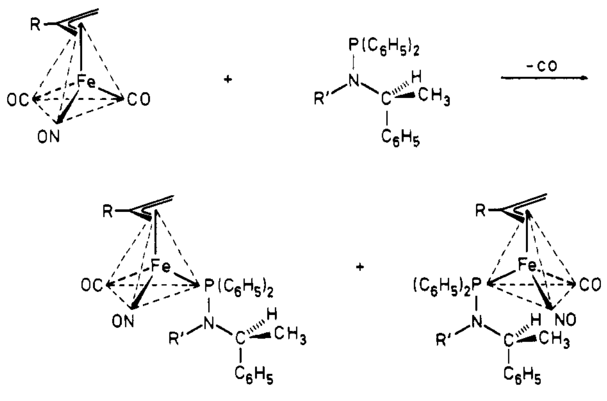
The complexes $(\eta^3\text{-}RC_3H_4)Fe(CO)(NO)(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$ (R, R′ = H, CH_3), 1-4, were synthesized by reaction of $(\eta^3\text{-}RC_3H_4)Fe(CO)_2NO$ with the corresponding (*S*)-aminophosphine. Two diastereoisomers, **b** (*RS*) and **a** (*SS*), differing only in the Fe configuration, were formed that could be separated by fractional crystallization and preparative liquid chromatography. The compounds are configurationally stable at the Fe atom up to 120 °C. The absolute configurations of diastereomers **1a** and **2b** have been determined by X-ray analysis. The conformations of a series of aminophosphine complexes are compared.

$(\eta^3\text{-}C_3H_5)Co[P(OCH_3)_3]_3$ is a homogeneous catalyst for the hydrogenation of aromatic hydrocarbons under mild reaction conditions.[2,3] $\sigma \rightleftarrows \pi$ allyl conversion and/or phosphite dissociation[4,5] is supposed to precede the activation of hydrogen at the Co center.

$(\eta^3$-allyl)Fe complexes are known for a variety of ligand combinations supplementing the iron shell to rare-gas configuration. In the compounds $(\eta^3\text{-}RC_3H_4)Fe(CO)(NO)P(C_6H_5)_3$[6-8] the Fe atom is an asymmetric center.[9] With the aminophosphine ligands $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$[10,11] (R′ = H, CH_3), derived from (*S*)-(−)-1-phenylethylamine instead of $P(C_6H_5)_3$, diastereoisomers should be formed that differ only in the Fe configuration.

Scheme I



1a,b, R = H, R′ = H; **2a,b**, R = H, R′ = CH_3; **3a,b**, R = CH_3, R′ = H; **4a,b**, R = CH_3, R′ = CH_3

After separation of the diastereomer, the stability of the Fe configuration with respect to epimerization and/or

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