Organometallics **1990**, *9*, 335-340

Isolation and Characterization of a Labile Intermediate in the Nucleophilic Attack of Hydride on a Chromium Diene Complex: $[NEt_4][Cr(CO)_3(P(OMe)_3)(\eta^3\text{-}(Z)\text{-}MeCHCHCH_2)]$

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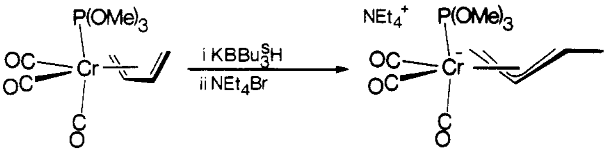
An intermediate in the reaction between potassium tri-*sec*-butylborohydride and (η^4-1,3-butadiene)-tricarbonyl(trimethyl phosphite)chromium(0) can be isolated after careful low-temperature workup, including counterion exchange. It is identified as the tetraethylammonium salt of the Z isomer of an η^3-2-buten-1-yl (*anti*-crotyl) complex. The compound crystallizes in the $P2_1/c$ space group with a = 13.705 (6) Å, b = 11.252 (3) Å, c = 14.490 (6) Å, β = 91.42 (3)°, and V = 2234 (2) Å^3. Refinement of 272 least-squares parameters using 2261 reflections with $I > 3.0\sigma(I)$ gave R = 3.5%, R_w = 4.5%. The solid-state structure confirms the stiochiometry of discrete tetraethylammonium cations and chromium complex anions. In contrast to most other open π-ligands in the $Cr(CO)_3L$ environment, the allyl lies with its open face *away* from the phosphite, a structure that persists in solution, as inferred from NMR studies. The complex is stable in CD_3CN and THF at −5 °C but isomerizes to the thermodynamically more stable E complex at ambient temperatures. The crystal structure of the diene starting material $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-butadiene) is also reported. It crystallizes in the $P2_1/c$ space group with a = 6.758 (5) Å, b = 27.27 (1) Å, c = 7.717 (4) Å, β = 91.42 (3)°, and V = 1373 (1) Å^3. Refinement of 163 least-squares parameters using 1498 reflections with $I >$ $3.0\sigma(I)$ gave R = 4.9%, R_w = 6.5%. The diene is oriented with the open face pointed toward the phosphite, as previously inferred from NMR data, and low-temperature NMR experiments with the diene complex indicate that the solid-state structure is retained in solution. These stereochemical results are consistent with initial hydride addition to generate a very unstable (Z)-allyl with its open face pointed toward the phosphite. Simple allyl rotation then occurs to give the observed product. Conversion to the thermodynamically more stable (E)-allyl then occurs through a π-σ-π rearrangement that also accomplishes an allyl rotation.

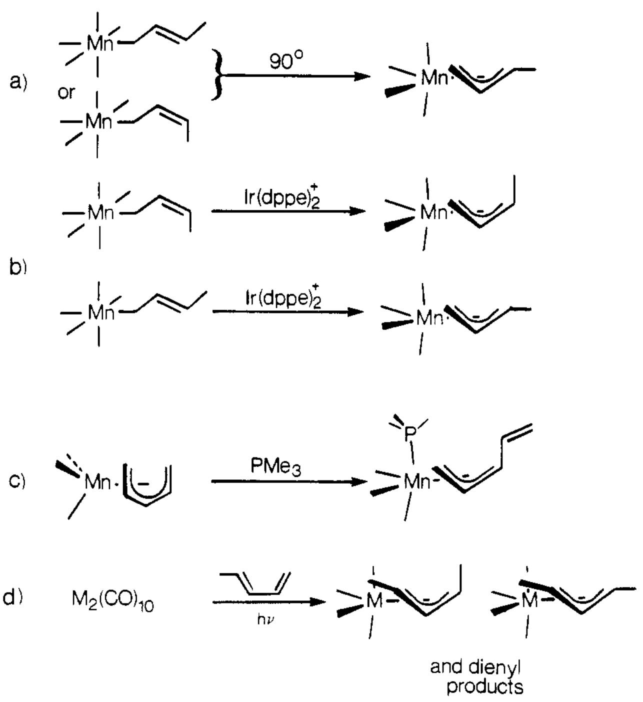
The addition of nucleophiles to coordinated π-ligands often gives a single stereoisomer kinetically and thermodynamically but in several important cases a subsequent rearrangement or isomerization occurs, including the migration of carbon nucleophiles from an internal to a terminal position of an iron-coordinated diene[1] and the occasional movement of nucleophiles among the carbons of a chromium-coordinated cyclohexadienyl.[2] We have been interested in the possibility that such a rearrangement may occur in the case of hydride addition to chromium diene complexes that, as we have shown,[3] yield E-substituted allyls as the thermodynamic product after workup and recrystallization (eq 1). The mechanism that we have assumed applies in this case is that the (S)-*cis*-diene ligand produces a (Z)-allyl that rearranges to the (E)-allyl product via a π–σ–π rearrangement.



(1)

One important problem with this mechanism is that there are several examples of closely related complexes where Z-substituted allyl ligands are stable to rearrangement at ambient temperature. For example, Druz' and co-workers have shown that, while thermal decarbonylation (ca. 90 °C) of either the E or Z isomer of $Mn(CO)_5(\sigma$-$CH_2CH{=}CHMe)$ gives exclusively the E isomer of the π-allyl complex (Scheme Ia),[4] room-temperature decarbonylation by $Ir(dppe)_2^+$ gives the corresponding (E)- or (Z)-π-allyl complex stereospecifically (Scheme Ib).[5] Powell and co-workers have also isolated an η^3-(Z)-allyl manganese complex through room-temperature reaction of a phosphine ligand with $Mn(CO)_3(\eta^5$-pentadienyl), which gives an η^3-pentadienyl complex with the pendant vinyl group

Scheme I. Routes to Substituted d^6 ML$_4$ Allyl Complexes



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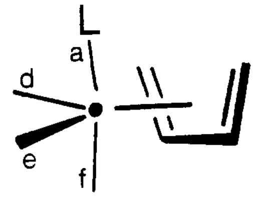

Figure 1. Nomenclature for positions of a $M(CO)_3L$(diene) complex.

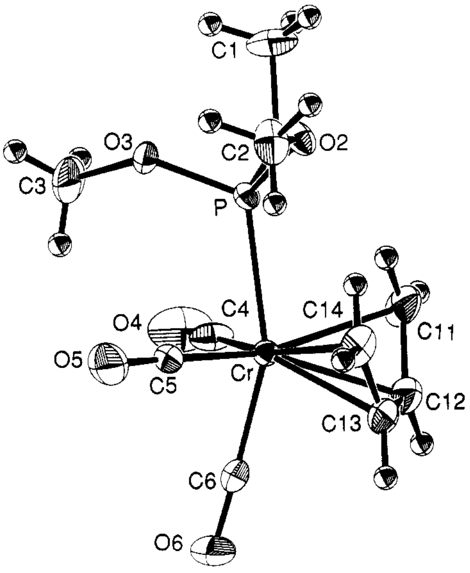

Figure 2. ORTEP drawing of the solid-state structure of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-butadiene), 1, with thermal ellipsoids at the 50% probability level; O(1) is obscured by C(2).

in the *Z* position (Scheme Ic).[6] No rearrangement is observed, and at higher temperatures CO is extruded and a substituted η^5-pentadienyl complex is formed. Such stereochemical integrity can also be inferred from the work of Kreiter and co-workers, where complexes of the stoichiometry $M(CO)_3L(\eta^3$-allyl) are found among the products of the photochemical reactions of manganese[7] and rhenium[8] carbonyls with dienes (Scheme Id). These are obtained as inseparable mixtures of *E* and *Z* isomers that are, apparently, stable to interconversion. In addition, several groups have examined the complex chemistry associated with addition of acids to iron dienes to produce iron allyls.[9] There, the complexity arises from the effects of coordinating counterions and agostic interactions that are critical in the mechanisms of rearrangements. Allyl ligands and their stereochemistry are also very important among the group 6 metals, though here the literature is dominated by complexes of the stoichiometry $(\eta^5\text{-}C_5H_5)MLL'(\eta^3$-allyl) that are stereochemically very different from our pseudooctahedral complexes.[10]

Table I. Experimental Details for Crystallographic Studies

	1	2
Crystal Data		
empirical formula	$C_{10}H_{15}CrO_6P$	$C_{25}H_{40}CrNO_6P$
formula wt	414.19	533.36
habit	yellow needle	yellow prism
size, mm	0.15 × 0.30 × 0.50	0.15 × 0.16 × 0.23
crys sys	monoclinic	monoclinic
lattice parameters		
a, Å	6.758 (5)	13.705 (6)
b, Å	27.27 (1)	11.252 (3)
c, Å	7.717 (4)	14.490 (6)
β, deg	105.22	91.42 (3)
vol, Å^3	1373 (1)	2234 (2)
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	4	4
D_{calc}	1.52 g cm^{-3}	1.31 g cm^{-3}
sys absences	$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$	
Intensity Measurements		
diffractometer	Rigaku AFC6S	
radiation	Cu Kα (λ = 1.54178 Å)	
temp, °C	−80 °C	
scan type	ω−2θ	
scan rate, deg min^{-1}	8.0	
F_{000}	648	1136
μ(Cu Kα), cm^{-1}	82.67	53.38
$2\theta_{max}$	110.4°	110.0°
data coll	$+h,+k,\pm l$	$+h,+k,\pm l$
rflcns measd	1956	3145
unique (R_{int})	1789 (0.055)	2996 (0.042)
trans factors for abs corr	0.75–1.46	0.83–1.43
Structure Solution and Refinement		
observations ($I > 3.00\sigma(I)$)	1498	2261
variables	163	272
reflctns/variable	9.2	8.3
residuals	R = 0.049, R_w = 0.065	R = 0.035, R_w = 0.045
goodness of fit	2.03	1.80
max peak in final difference map, e Å^{-3}	0.4	0.3
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ $w = 4F_o^2/\sigma^2(F_o)$	

These results highlight the apparent uniqueness of the facile formation of a thermodynamically stable (*E*)-allyl complex is our systems[3] and raise significant questions about the mechanism of nucleophilic attack. In this paper, we report the synthesis and isolation of an important intermediate in the synthesis of (*E*)-allyl complexes, a π-allyl complex with the methyl group in the *Z* position. This complex readily produces the corresponding *E* isomer at ambient temperatures and is subject to stereospecific cleavage by acid.

Results

Solid-State and Solution Structure of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-butadiene), 1. One important question about the mechanism of allyl anion formation is the actual structure of the starting diene complex. Kreiter, in his definitive work on pseudooctahedral diene complexes, has presented compelling evidence that the ground-state structure of complex 1 (and most other pseudooctahedral diene complexes) is *facial* with the diene almost always oriented such that its open face points at an axial position occupied by L (Figure 1).[11,12] Crystallographic confirmation of this assignment is given by an X-ray diffraction

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(12) Conventional nomenclature denotes the apical position when the open π-ligand is drawn with its open face up as the *a* position.

Table II. Positional and Isotropic Thermal Parameters for $Cr(CO)_3(P(OMe)_3)$(1,3-butadiene)

atom	*x*	*y*	*z*	*B*(eq)
Cr	0.4387 (1)	0.09825 (3)	0.1958 (1)	1.20 (4)
P	0.2534 (2)	0.15567 (5)	−0.0009 (2)	1.30 (5)
O(1)	0.2210 (5)	0.2060 (1)	0.0936 (5)	1.9 (1)
O(2)	0.0207 (5)	0.1449 (1)	−0.1117 (4)	1.8 (1)
O(3)	0.3377 (5)	0.1727 (1)	−0.1681 (4)	1.9 (1)
O(4)	0.7178 (7)	0.1828 (2)	0.3390 (6)	4.6 (2)
O(5)	0.5716 (6)	0.0625 (2)	−0.1224 (6)	3.3 (2)
O(6)	0.8090 (6)	0.0397 (2)	0.3922 (6)	3.3 (2)
C(1)	0.104 (1)	0.2458 (2)	−0.0076 (8)	3.0 (2)
C(2)	−0.0204 (8)	0.1118 (2)	−0.2636 (7)	2.6 (2)
C(3)	0.5410 (9)	0.1924 (3)	−0.144 (1)	3.7 (3)
C(4)	0.6108 (8)	0.1507 (2)	0.2779 (7)	2.2 (2)
C(5)	0.5209 (7)	0.0771 (2)	0.0006 (7)	1.7 (2)
C(6)	0.6659 (8)	0.0618 (2)	0.3194 (7)	2.1 (2)
C(11)	0.220 (1)	0.1231 (2)	0.3571 (8)	3.0 (3)
C(12)	0.3028 (9)	0.0776 (2)	0.4104 (8)	2.7 (2)
C(13)	0.2750 (8)	0.0383 (2)	0.2852 (8)	2.3 (2)
C(14)	0.1668 (8)	0.0460 (2)	0.1092 (8)	2.5 (2)

Table III. Intramolecular Distances (angstroms) and Angles (degrees) for $Cr(CO)_3(P(OMe)_3)$(η-1,3-butadiene)

atom	atom	distance	atom	atom	distance
Cr(1)	P(1)	2.309 (2)	Cr(1)	C(13)	2.183 (5)
Cr(1)	C(4)	1.849 (6)	Cr(1)	C(14)	2.282 (5)
Cr(1)	C(5)	1.829 (6)	C(11)	C(12)	1.381 (8)
Cr(1)	C(6)	1.867 (6)	C(12)	C(13)	1.420 (8)
Cr(1)	C(11)	2.275 (6)	C(13)	C(14)	1.380 (8)
Cr(1)	C(12)	2.170 (6)			

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Cr(1)	C(4)	83.4 (2)	Cr(1)	C(4)	O(4)	176.4 (5)
P(1)	Cr(1)	C(5)	84.3 (2)	Cr(1)	C(5)	O(5)	178.1 (5)
P(1)	Cr(1)	C(6)	158.2 (2)	Cr(1)	C(6)	O(6)	178.1 (5)
C(4)	Cr(1)	C(5)	103.2 (2)	Cr(1)	C(11)	C(12)	67.8 (3)
C(4)	Cr(1)	C(6)	83.0 (2)	Cr(1)	C(12)	C(11)	76.1 (3)
C(5)	Cr(1)	C(6)	82.4 (2)	Cr(1)	C(12)	C(13)	71.4 (3)
C(11)	Cr(1)	C(12)	36.1 (2)	Cr(1)	C(13)	C(12)	70.5 (3)
C(11)	Cr(1)	C(13)	66.0 (2)	Cr(1)	C(13)	C(14)	76.0 (3)
C(11)	Cr(1)	C(14)	75.9 (2)	Cr(1)	C(14)	C(13)	68.1 (3)
C(12)	Cr(1)	C(13)	38.1 (2)	C(11)	C(12)	C(13)	120.1 (5)
C(12)	Cr(1)	C(14)	65.9 (2)	C(12)	C(13)	C(14)	120.0 (5)
C(13)	Cr(1)	C(14)	35.9 (2)				

and low-temperature NMR study. Experimental details for the X-ray diffraction study of 1 are given in Table I. The structure of the compound, with atomic numbering for the non-hydrogen atoms, is shown in Figure 2. Atomic positions for the non-hydrogen atoms are given in Table II, and important bond lengths and angles are given in Table III. The phosphite is clearly in the *a* position of a distorted octahedron. The two axial ligands are bent back significantly, with a P–Cr–C(6) angle of 158.2 (2)°; the two equatorial ligands are, in turn, moved away from each other (to an angle of 103.1 (2)°). The geometry of diene coordination has the two internal carbon atoms 0.1 Å closer to the metal than the two terminal carbons, resulting in a tilted orientation. The structure is quite similar to that for $Cr(CO)_2(PMe_3)_2(\eta^4$-(*E*,*E*)-2,4-hexadiene) reported by Kreiter and Bau[13] and seems to be similar to a monophosphite tungsten derivative illustrated by Kreiter in his review.[11,14]

Table IV. ^1H NMR Resonances (ppm) for Allyl Groups in *f*-*Z* (2) and *a*-*E* (3) Complexes[a]

	f-*Z* (d_8-THF)	*a*-*E* (CD_3CN)
1-*Z*-H	1.55	0.60
1-*E* H	1.93	1.38
2 H	4.20	4.38
3 H	2.80 (*E*)	1.73 (*Z*)
3 CH_3	1.21 (*Z*)	1.58 (*E*)

[a] There are relatively small (1 ppm) changes in peak positions between THF and CD_3CN, which justifies this qualitative comparison.

Observation of a solid-state structure does not confirm the solution structure, of course, especially since these diene derivatives are known to undergo effective rotation in solution. However, the rates of rotation are such that they ought to be *chemically* slow at low temperatures, and an NMR spectrum on material dissolved into d_8-toluene at −40 °C shows that the room-temperature pattern is present. This gives added confidence to the assumption that the *a* isomer is present in solution when nucleophilic attack is carried out.

Synthesis and Isolation of a Thermodynamically Unstable Product of Nucleophilic Attack. Addition of a stoichiometric amount of potassium tri-*sec*-butylborohydride (K-Selectride) to a THF solution of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-butadiene) immersed in a dry ice/2-propanol bath produces a milky white yellow suspension. Counterion exchange is accomplished by the addition, through the top of the Schlenk flask against a positive flow of nitrogen, of an excess of oven-dried NEt_4Br. The solution is stirred vigorously overnight and carefully filtered through a filter stick[16] wrapped in dry ice. Addition of a layer of diethyl ether initiates the crystallization of product 2, which is completed during storage in a freezer at ca. −20 °C. After removal of the supernatant and drying in vacuo, the solids are collected as yellow crystals in fair yield (50–60%). These crystals are suitable for spectroscopic analysis, combustion analysis, and X-ray diffraction studies without further purification. They are stable indefinitely in the solid state at low temperature (ca. −40 °C) and are moderately stable at room temperature.

An NMR spectrum of the product of low-temperature workup, 2, is clearly different from that observed for the thermodynamic product 3. Complete assignment is possible in THF-d_8 and a comparison of the shifts for the two isomers is presented in Table IV. The differences in the spectra of the two isomers are essentially as expected. For example, comparison of the spectra the *a* and *f* isomers of $Cr(CO)_3(P(OMe)_3)$((*E*,*E*)-η^4-2,4-hexadiene), which are both present in solution,[17] shows that proximity to the phosphite results in a shift to lower δ, precisely the effect seen in comparing the hydrogens at the 2-position (closer to the phosphite in the *f* isomer) and at the 1-position (closer to the phosphite in the *a* isomer).

X-ray Crystallographic Study of the (*Z*)-Allyl Product. The structure of the allyl anion 2 was confirmed by an X-ray crystallographic study with experimental details given in Table I. The structure of the anion, with atomic numbering for the non-hydrogen atoms, is shown in Figure 3. Atomic positions for the non-hydrogen atoms

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(14) This bend-back angle is probably controlled by the π-acceptor capability of the hydrocarbon ligand. Conjugated dienes are relatively good π-acceptors and, therefore, favor a distortion of the other ligands to produce a relatively high lying occupied orbital on the ML_4 fragment, which occurs when the ML_4 fragment distorts significantly. This is also seen in the structure of $Cr(CO)_2(P(OMe)_3)_2(\eta^2$-diphenylacetylene).[15] With allyl ligands (when treated as closed-shell anions) there is little if any π-acceptor capability, consistent with the relatively *un*distorted ML_4 geometry.

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Table V. Positional and Isotropic Thermal Parameters for $[NEt_4][Cr(CO)_3(P(OMe)_3)(\eta^3\text{-}(Z)\text{-2-buten-1-yl})]$

atom	*x*	*y*	*z*	*B*(eq)
Cr	0.27577 (4)	0.11922 (5)	0.14509 (4)	1.54 (3)
P	0.15731 (6)	0.04852 (9)	0.23814 (6)	1.74 (4)
O(1)	0.0442 (2)	0.0739 (2)	0.2099 (2)	2.2 (1)
O(2)	0.1562 (2)	−0.0930 (2)	0.2554 (2)	2.3 (1)
O(3)	0.1495 (2)	0.0898 (2)	0.3443 (2)	2.6 (1)
O(4)	0.2104 (2)	−0.0313 (2)	−0.0137 (2)	3.0 (1)
O(5)	0.1313 (2)	0.3128 (2)	0.1058 (2)	2.8 (1)
O(6)	0.3987 (2)	0.2323 (3)	0.0002 (2)	3.3 (1)
N	0.7210 (2)	0.1117 (3)	0.4130 (2)	1.8 (1)
C(1)	0.0084 (3)	0.0451 (4)	0.1190 (3)	2.7 (2)
C(2)	0.0762 (3)	−0.1488 (4)	0.3028 (3)	3.1 (2)
C(3)	0.1562 (3)	0.2141 (4)	0.3657 (3)	3.0 (2)
C(4)	0.2331 (2)	0.0266 (3)	0.0511 (3)	1.8 (2)
C(5)	0.1903 (3)	0.2383 (3)	0.1230 (2)	1.8 (2)
C(6)	0.3554 (3)	0.1866 (3)	0.0586 (3)	2.1 (2)
C(11)	0.3894 (3)	0.1937 (4)	0.2507 (3)	2.6 (2)
C(12)	0.3741 (3)	0.0738 (4)	0.2588 (3)	2.4 (2)
C(13)	0.3930 (3)	−0.0139 (4)	0.1921 (3)	2.4 (2)
C(14)	0.4816 (3)	−0.0136 (5)	0.1336 (3)	3.4 (2)
C(51)	0.7233 (3)	0.1340 (4)	0.3102 (3)	2.7 (2)
C(52)	0.7679 (3)	0.0360 (4)	0.2549 (3)	4.0 (2)
C(53)	0.8233 (3)	0.0918 (3)	0.4531 (3)	2.1 (2)
C(54)	0.8940 (3)	0.1933 (4)	0.4396 (3)	3.5 (2)
C(55)	0.6643 (3)	−0.0010 (3)	0.4342 (2)	2.0 (2)
C(56)	0.5621 (3)	−0.0042 (4)	0.3929 (3)	3.0 (2)
C(57)	0.6731 (3)	0.2195 (3)	0.4560 (3)	2.7 (2)
C(58)	0.6694 (3)	0.2197 (4)	0.5588 (3)	3.3 (2)

Table VI. Selected Intramolecular Distances (angstroms) and Angles (degrees) for $[NEt_4][Cr(CO)_3(P(OMe)_3)(\eta\text{-}(Z)\text{-2-buten-1-yl})]$

atom	atom	dist	atom	atom	dist
Cr	P	2.279 (1)	C(11)	C(12)	1.371 (6)
Cr	C(4)	1.801 (4)	C(12)	C(13)	1.410 (6)
Cr	C(5)	1.804 (4)	C(13)	C(14)	1.499 (6)
Cr	C(6)	1.845 (4)	Cr	C(11)	2.313 (4)
Cr	C(12)	2.164 (4)	Cr	C(13)	2.287 (4)

atom	atom	atom	angle	atom	atom	atom	angle
P	Cr	C(4)	91.3 (1)	Cr	C(4)	O(4)	175.5 (3)
P	Cr	C(5)	84.0 (1)	Cr	C(5)	O(5)	176.7 (3)
P	Cr	C(6)	170.8 (1)	Cr	C(6)	O(6)	174.3 (3)
C(4)	Cr	C(5)	95.6 (2)	C(11)	C(12)	C(13)	126.8 (4)
C(4)	Cr	C(6)	84.9 (2)	C(12)	C(13)	C(14)	123.5 (4)
C(5)	Cr	C(6)	88.1 (2)				

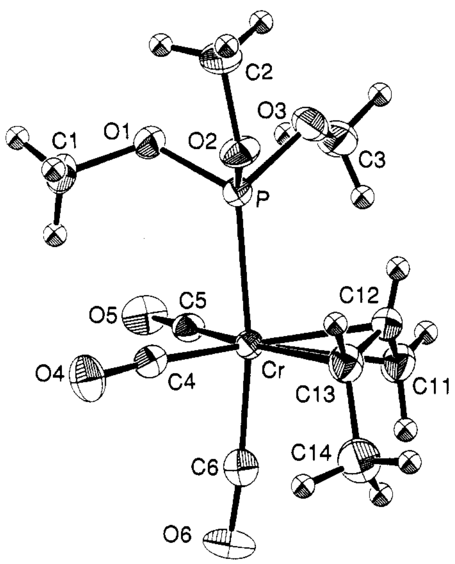

Figure 3. ORTEP drawing of the solid-state structure of the anion in $[NEt_4][a\text{-}Cr(CO)_3(P(OMe)_3)(\eta^3\text{-}(Z)\text{-2-buten-1-yl}]$, **2**, with thermal ellipsoids at the 50% probability level.

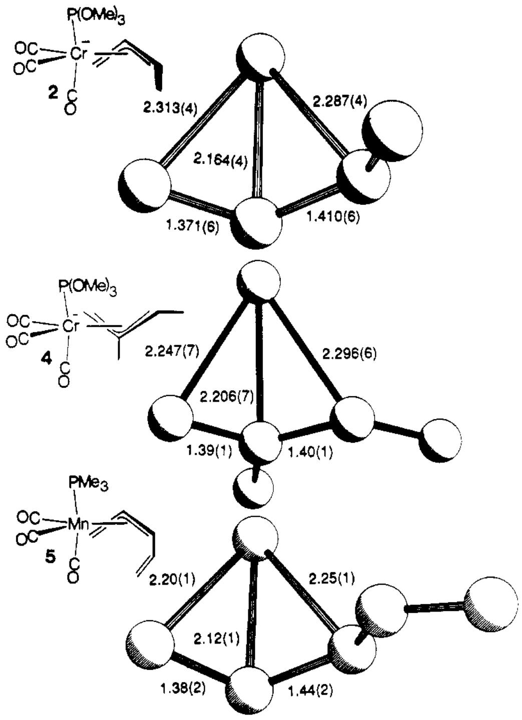

Figure 4. Comparison of allyl–metal bonding in $[f\text{-}Cr(CO)_3(P(OMe)_3)((Z)\text{-2-buten-1-yl})]$, **2**; $[a\text{-}Cr(CO)_3(P(OMe)_3)(2\text{-methyl-}(E)\text{-2-buten-1-yl})]$, **4**, and $f\text{-}Mn(CO)_3(PMe_3)(\eta^3\text{-}(Z)\text{-pentadienyl})$, **5**.

and the hydrogen atoms of the allyl ligand are given in Table V, and important bond lengths and angles are presented in Table VI. The structure confirms the *Z* stereochemistry of the allyl and shows that the phosphite is in the *f* position, *away* from the open face of the allyl ligand.

Several other important features of the metal–allyl bonding are best understood in comparison with the structure of the (*E*)-allyl in $[NEt_4][Cr(CO)_3(P(OMe)_3)((E)\text{-}\eta^3\text{-2-methyl-2-buten-1-yl})]$, **4**,[3] and the (*Z*)-allyl in $Mn(CO)_3(PMe_3)((Z)\text{-}\eta^3\text{-2,4-butadien-1-yl})$, **5**.[6] The former compound is found in the *a* rotamer in the solid state, and this predominates in the reaction mixture. The latter complex exists solely in the *f* rotamer. Important features of the metal–allyl interactions for all three compounds are given in Figure 4.

The allyl ligand in all three complexes is bonded with shorter distances to the central carbon, a common feature of allyl bonding.[18] There is also a statistically significant asymmetry of the distances to the terminal carbons. In the case of the two stable allyl complexes, **4** and **5**, the unsubstituted carbon is closer to the metal but in the case of the unstable allyl **2** it is farther away. Tentatively, we suggest that the increased bond length to the unsubstituted carbon in **2** indicates that the allyl is more ready to open up to a σ-allyl, as required for rearrangement (vide infra). The carbon bound to the allyl is swung well out of the allyl plane, with C11–C12–C13–C14 torsion angle of 40°. This is not simply pyramidalization, for the corresponding torsion angle of the (independently refined) *Z* hydrogen on the other terminal position is 30°. A similar distortion is seen in for the *Z* substituent in **5** (torsion angle 45°). These can be compared with the terminal methyl group

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(18) Exceptions have been observed when there are substituents in the 2-position Murral, N. W.; Welch, A. J. *Acta Crystallogr.* **1984**, *C40*, 401), in certain early transition metal systems, such as titanium (Helmholdt, R. B.; Jellinek, F.; Martin, H. A.; Vos., A. *Recuil* **1967**, *86*, 1263), and with η^3-benzyl systems (Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.

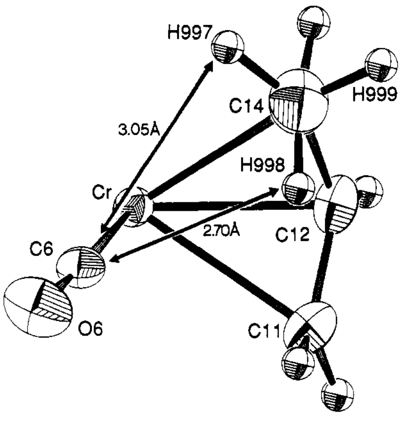
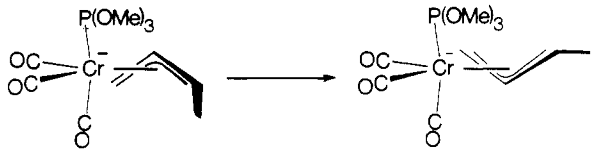


Figure 5. View of chromium-(*Z*)-allyl structure along C(14)–C(13) illustrating the close contact between the methyl group and C(6) and the eclipsing of the C(12)–C(13) bond by a methyl group hydrogen.

in 4, which is essentially coplanar with the three allyl carbons. Such out-of-plane distortions have been observed in other metal ligand environements, for example, in a *Z*-substituted molybdenum cyclopentadienyl allyl complex.[10b]

Another indication of intramolecular steric crowding in 2 is the orientation of the methyl group hydrogens. These were refined independently after they appeared *away* from calculated positions (which minimize normal steric interactions on the ligand). Instead, the methyl hydrogens lie in a way that forces one to approximately eclipse a carbon–carbon bond (Figure 5). This minimizes interactions with the chromium and its substituents. The nearest contact to C6 is 2.70 Å in the refined structure, while the calculated positions would put on of the methyl hydrogens within 2.33 Å of C6.

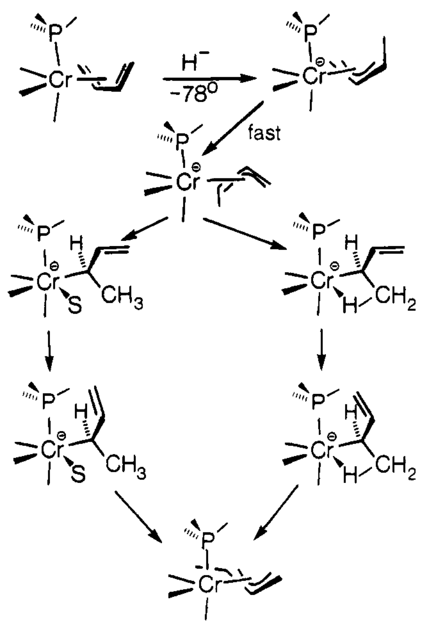
Stereospecific Allyl Isomerization and Electrophilic Cleavage. The *Z* isomer 2 readily isomerizes to the *E* isomer 3 in either CD_3CN or d_8-THF solution at room temperature (eq 2). In both cases the disappearance of 2 is apparently first order over 2 half-lives with a faster rate in CD_3CN (15×10^{-6} s^{-1}) than in d_8-THF (8×10^{-6} s^{-1}). But both reactions are accompanied by some decomposition to olefinic products and solids, and it is therefore inappropriate to draw detailed conclusions about the kinetics of the reaction, except to note that there are *no* resonances observed for other allyl complexes.

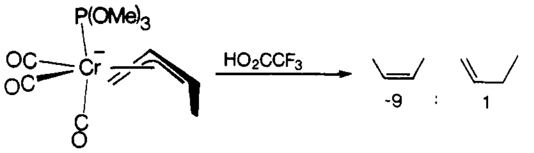


(2)

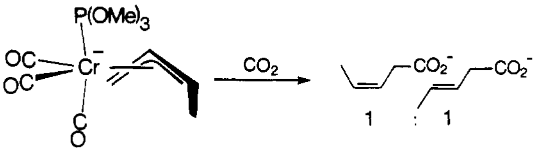
Electrophilic cleavage of the thermodynamically more stable (*E*)-allyl complex gives functionalized olefins that are exclusively the product of electrophilic attack at the least substituted carbon with retention of the *E* stereochemistry.[3,19] The (*Z*)-allyl complex similarly reacts rapidly (in seconds) and apparently quantitatively in CD_3CN with HO_2CCF_3 to give a preponderance of *cis*-2-butene, along with a small (ca. 10%) amount of 1-butene (eq 3). With carbon dioxide a somewhat slower reaction (minutes) occurs to give a complex mixture of products. A low-temperature experiment shows that the process of adding CO_2 to the solution causes the formation of a considerable amount of 2-butene and then, at higher temperatures, electrophilic cleavage to a mixture of *cis*- and *trans*-3-pentenoate occurs (eq 4).

Scheme II. Proposed Mechanism of *Z* to *E* Syn Isomerization with Possible Solvent Assistance (Left Pathway) or Agostic Intermediate (Right Pathway)





(3)



(4)

Discussion

Stereochemistry of Allyl Anion Formation and Rotation. The mechanism that we suggest for the overall transformation of a diene ligand to an *E*-substituted allyl is shown in Scheme II and incorporates two of three possible mechanisms for allyl rotation.[20] There are several examples of allyl rotation that occurs simply (i.e., with the η^3 bonding intact throughout),[21] including, most importantly, the d^6 pseudooctahedral complexes $Fe(CO)_3X(\eta\text{-}C_3H_5)$ (X = halide, NCO),[9a] which are isoelectronic with our $Cr(CO)_3(P(OMe)_3)(\eta^3\text{-allyl})$ complexes. In certain other cases allyl rotation seems to occur with opening of the allyl system to a σ-allyl, which can also interconvert *E*/*Z* positions and chirality about the metal.[22] However, Basolo has offered convincing evidence that π–σ–π rearrangements are not involved in the CO substitution reactions of $Mn(CO)_4(\eta\text{-}C_6H_5)$, suggesting that this is a relatively high-energy process in the d^6 ML_4(allyl) environment.[23]

The mechanism we suggest for our reaction begins with addition of the hydride to the coordinated diene at −78 °C. This rapid reaction should give, as a kinetic product, the

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[19] Wink, D. J.; Wang, N.-F., research in progress.

[20] (a) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (b) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; pp 441–488.

[21] A general listing, still essentially current, is provided in Table III of Faller's review.[20a]

[22] Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 155.

[23] Palmer, G. T.; Basolo, F. *J. Am. Chem. Soc.* **1985**, *107*, 3122.

the severely crowded *a* isomer of the (*Z*)-allyl. Simple allyl rotation, while not normally rapid, will minimize the repulsion of the *Z*-disposed methyl group and the phosphite and create the isolated *f* isomer **2**. The π to σ transformation of **2** to **3** is coupled to allyl rotation via a formally five-coordinate complex that is stereochemically stable. A coordinating solvent or an agostic interaction would provide the stability.

There remains the significant question of why this process occurs with $Cr(CO)_3L(\eta^3$-allyl) anions but not with other isoelectronic complexes. One is tempted to use steric arguments, since there are several indications that these molecules are quite crowded. However, the relatively more crowded manganese and iron complexes are quite stable to rearrangement. Thus, we believe there may be an electronic explanation for the lability of the chromium anion **2**. Substitution in the *Z* position forces a *sterically induced* pyramidalization of the allyl carbon and will make it a better donor to the metal. This will be less favorable in an anionic complex than in a neutral one and, therefore, could serve to make a π–σ–π rearrangement (which would relieve the induced pyramidaliazation) much more facile.

Experimental Section

Synthesis of Tetraethylammonium (η^3-(*Z*)-2-Buten-1-yl)tricarbonyl(trimethyl phosphite)chromium(1^-). A solution of 1.05 g (3.3 mmol) of $Cr(CO)_3(P(OMe)_3)(\eta^4\text{-}1,3\text{-}C_4H_6)$ in 20 mL of THF was cooled in a dry ice/2-propanol bath. $KB(s\text{-}Bu)_3H$ (1 equiv, 3.3 mL, Aldrich, 1.0 M in THF) was added via syringe, and the solution was stirred until a milky precipitate formed, about 20 min. An excess of NEt_4Br was added through the neck of the Schlenk flask against a positive flow of nitrogen. The mixture was vigorously stirred overnight in the dry ice bath. The yellow supernatant was removed from the fine white solids by filtration through a "filter stick" with the Teflon transfer tube wrapped in a dry ice filled towel. The product was crystallized by the slow admixture (3 days) at ca. −20 °C of an equal volume of ether. Fine yellow crystals (0.85 g, 57%) of spectroscopically and analytically pure $[NEt_4][Cr(CO)_3(P(OMe)_3)(\eta^3\text{-}(Z)\text{-}2\text{-buten-}1\text{-yl})]$ were collected by decanting the supernatant at dry ice temperature and drying in vacuo; ^1H NMR (CD_3CN, −5 °C) δ 4.26–4.12 (m, H^2), 3.40 (d, $P(OCH_3)_3$), 3.15 (qu, NCH_2CH_3), 2.82 (qn, $H^{3,E}$), 1.45 (m, $H^{1,Z}$), 1.20 (t of t, NCH_2CH_3); ^1H NMR (C_4D_8O, −5 °C) δ 4.26–4.12 (m, H^2), 3.40 (m, $P(OCH_3)_3$ and NCH_2CH_3), 2.80 (m, $H^{3,E}$), 1.93 (d, $H^{1,E}$), 1.55 (m, $H^{1,Z}$), 1.35 (t of t, NCH_2CH_3), 1.21 (d, (*Z*)-CH_3); ^{13}C NMR (CD_3CN, −5 °C) δ 92.68 (C(2)), 53.4 (C(3)), 51.92 ($P(OCH_3)$), 49.80 (CH_2CH_3), 35.99 (C(1)), 19.33 (allyl CH_3), 6.72 (CH_2CH_3); ^{31}P NMR (CD_3CN, ambient) δ 199.1. Anal. Calcd for $C_{18}H_{36}CrNPO_6$: C, 48.54; H, 8.15. Found (Schwarzkopf): C, 49.09; H, 8.33.

X-ray Crystallography. A tabulation of most of the experimental details is provided in Table I. The crystals were mounted on a glass fiber under a flow of cold nitrogen gas and then transferred to the goniostat, which was equipped with a flow of nitrogen regulated at −80 °C. Cell constants and an orientation matrix for data collection were obtained from the setting angles of 25 reflections in the range $30.3 < 2\theta < 35.0°$. The Laue group was confirmed by a check of equivalent reflections. The space group was determined by an examination of systematic absences[24] and confirmed by successful solution and refinement of the structure. There was no significant decay in three check reflections, and the data were used directly. Structure solution was by Patterson methods[25] to locate the chromium, accompanied by direct-methods analysis to find the remaining non-hydrogen atoms.[26] After isotropic refinement of the structure, an empirical absorption correction was applied.[27]

For (η^4-1,3-butadiene)tricarbonyl(trimethylphosphite)chromium(0), anisotropic refinement of all non-hydrogen atoms was done with all hydrogens in calculated positions. In the case of tetraethylammonium (η^3-(*E*)-2-buten-1-yl)tricarbonyl(trimethylphosphite)chromium(1−), all hydrogen atoms on the allyl ligand were refined independently. The refined positions are all chemically reasonable, with the exception of a short (0.80 Å) C–H bond at the 2-position. After convergence, the largest peaks in the Fourier difference map (0.3 e $Å^{-3}$) occurred in the vicinity of one of the phosphite methyl groups.

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Supplementary Material Available: Tables of the hydrogen atom positional and thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, complete bond distances and angles, torsional angles, and relevant least-squares planes, drawings of atomic packing for **1** and **2**, and a drawing of the complete asymmetric unit for **2** (16 pages); listings of observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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(24) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(25) PHASE, Patterson Heavy Atom Solution Extractor: Calabrese, J. C. Ph.D. Thesis, University of Wisconsin - Madison, 1972.

(26) DIRDIF: Beurskens, P. T. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(27) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.