Summary

Observations on olefin/SiH_4 reactions (olefin isomerization, alkylsilane formation) are consistent with Barton mechanisms involving silacyclopropane and alkylsilylene intermediates. SCP ring-forming and -opening reactions are at least an order of magnitude faster than their decompositions (to olefins and SiH_2). All reactions are pressure dependent at 400 Torr. On the basis of butylsilylene- and pentylsilylene-trapping reactions with silane of 4.8×10^9 M^{-1} s^{-1} and 3.1×10^9 M^{-1} s^{-1}, respectively, high-pressure Arrhenius parameters for the butyl- and pentysilylene decompositions of $\log A_\infty = 15.5 \pm 1$ and $E_\infty = 22.5 \pm 0.3$ kcal are derived. Activation energies are consistent with decomposition reaction thermochemistries ($\Delta H_{dec} = 26.6 \pm 3.4$ kcal, $\Delta E_{dec} = 25.3 \pm 3.4$ kcal), and *A* factors indicate surprisingly loose transition states for both alkysilylene decompositions and their reverse silylene/olefin additions. A loose silylene/olefin addition complex is suggested for the transition state, as the thermochemistry of decomposition precludes the intermediacy of biradicals. Generic high-pressure Arrhenius parameters (with *A* in s^{-1}, *E* in kcal) for the elementary reactions of silacyclopropane ring opening (o), closing (c), and decomposition (d) are $\log A_c = 12.3$, $E_c = 10.4$; $\log A_o = 14.0$, $E_o = 14.7 + \Delta E$; and $\log A_d = 16.9$, $E_d = 26.1 + \Delta E$, where $\Delta E = (49.6 - \text{SCP strain energy})$.

Acknowledgment. We are indebted to the National Science Foundation (Grants CHE-8419089 and CHE-8719843) for financial support of this work.

Registry No. Silane, 7803-62-5; 1-butene, 106-98-9; 1-pentene, 109-67-1; 4-methyl-1-pentene, 691-37-2; 2-pentene, 109-68-2; 2-methyl-2-pentene, 625-27-4; disilane, 1590-87-0; 2-butylsilylene, 110550-55-5; isopentylsilylene, 135710-28-0; silylene, 13825-90-6; 2-methyl-1-pentene, 763-29-1.

Organochromium π-Complexes. 3.[1,2] Preparation and Reactions of Bis(η^3-allyl)chromium(II) Complexes

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$Cr(PR_3)_2Cl_2$ (PR_3 = PMe_3, PMe_2Ph, PPh_2Me), $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$, and $[Cr(Pr^i_2PC_2H_4PPr^i_2)Cl_2]_2$ react with 2-propenylmagnesium chloride or 2-methyl-2-propenylmagnesium chloride to give thermolabile $(\eta^3\text{-allyl})_2Cr(PR_3)_2$ and $(\eta^3\text{-allyl})_2Cr(R_2PC_2H_4PR_2)$ compounds. In contrast, the final product of the reaction between $Cr(PMe_3)_2Cl_2$ and 2-butenylmagnesium chloride contains an η^2,η^2-bonded dimethyldiallyl group derived from the reductive coupling of two η^3-1-MeC_3H_4 fragments. $(\eta^3\text{-}C_3H_5)_2Cr(PMe_3)_2$ reacts with 2-butyne with alkyne insertion into an η^3-allyl group to give a compound containing both η^3-allyl and η^1,η^2-4-methyl-1,4-hexadienyl groups. The structures of these paramagnetic organochromium(II) compounds have been confirmed by X-ray structural determinations of three examples, viz. $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (**2**) (*a* = 8.894 (4) Å, *b* = 27.56 (1) Å, c = 9.355 (3) Å, *β* = 107.64 (3)°, space group $P2_1/n$, *Z* = 4), $(\eta^3\text{-}C_3H_5)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$ (**6**) (*a* = 9.171 (1) Å, *b* = 15.936 (2) Å, *c* = 15.368 (1) Å, *β* = 102.22 (1)°, space group $P2_1/n$, *Z* = 4) and $(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2\text{-4-methyl-1,4-hexadienyl})Cr(PMe_3)_2$ (**9**) (*a* = 9.299 (5) Å, *b* = 14.474 (8) Å, *c* = 13.916 (5) Å, space group $P2_12_12_1$, *Z* = 4).

Introduction

Although the organic compounds of chromium have not attained industrial importance as homogeneous catalysts, it has been known for over a quarter of a century that species containing the η^3-allyl group do have considerable activity. For example, $(\eta^3\text{-}C_3H_5)_3Cr$ attracted attention in the late 60's as a non-Ziegler catalyst for the polymerization of ethylene and butadiene while $[(\eta^3\text{-}C_3H_5)_2CrI]_2$ cyclotrimerizes butadiene to cyclododecatriene.[3-5] Subsequently, it was shown that η^3-allyl–chromium species catalyze the cyclotrimerization of alkynes[6] as well as the polymerization of acrylonitrile, methyl methacrylate, and substituted 1,3-dienes[7] while dozens of publications have been concerned with the catalytic activity of supported η^3-allyl–Cr catalysts.

Examples of *mononuclear* η^3-allyl complexes of chromium are, however, limited to those containing Cr(III) or Cr(I), e.g. $(\eta^3\text{-}C_3H_5)_3Cr$,[3] $Cp(\eta^3\text{-}C_3H_5)_2Cr$,[1] and $(\eta^3\text{-}C_3H_5)(\eta^4\text{-1-}EtC_4H_5)Cr(Me_2PC_2H_4PMe_2)$,[2] and as far as we are aware, no compounds of this type containing Cr(II) have been reported in the literature. Attempts to prepare such compounds by reacting the dinuclear species $(\eta^3\text{-}C_3H_5)_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2Cr_2$ with donor ligands were not successful.[8] On the other hand a few bis(aryl)- and bis(alkyl)–Cr(II) complexes, e.g. $(2,4,6\text{-}Me_3C_6H_2)_2Cr(PR_3)_2$,[9,10] $(Me_3CCH_2)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$,[10] and $Me_2Cr(Me_2PC_2H_4PMe_2)_2$,[11,12] have been prepared by reacting

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* To whom correspondence should be addressed.

(1) Part 1: Angermund, K.; Döhring, A.; Jolly, P. W.; Krüger, C.; Romão, C. C. *Organometallics* 1986, *5*, 1268.

(2) Part 2: Iczek, F.; Jolly, P. W.; Krüger, C. *J. Organomet. Chem.* 1990, *382*, C11.

(3) Oberkirch, W. Dissertation, Techn. Hochschule Aachen, 1963.

(4) Studiengesellschaft Kohle m.b.H. Neth. Appl. 6,409,179, 1963/5; *Chem. Abstr.* 1965, *63*, 5770h.

(5) Wilke, G.; Bogdanovič, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* 1966, *78*, 157.

(6) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* 1971, 28, 259.

(7) Ballard, D. G. H. *Adv. Catal.* 1973, *23*, 263.

(8) See, for example: Zimmermann, K. Dissertation, Friedrich-Schiller-Universität, Jena, Germany, 1971.

(9) Seidel, W.; Stoll, G. *Z. Chem.* 1974, *14*, 488.

(10) Hermes, A. R.; Morris, R. J.; Girolami, G. S. *Organometallics* 1988, *7*, 2372.

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Table I. Selected Structural Parameters for $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (2) and $(\eta^3\text{-}C_3H_5)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$ (6)

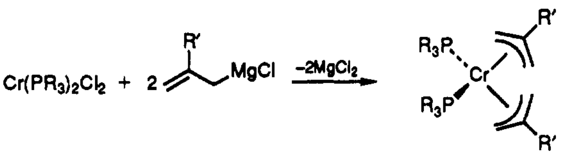
	2	6
Bond Distances (Å)		
Cr–D(1)	1.877	1.926
Cr–D(2)	1.920	1.924
Cr–P(1)	2.425 (1)	2.415 (1)
Cr–P(2)	2.412 (1)	2.416 (1)
Cr–C(1)	2.211 (5)	2.205 (2)
Cr–C(2)	2.082 (5)	2.145 (1)
Cr–C(3)	2.166 (5)	2.229 (2)
Cr–C(4)	2.233 (4)	2.231 (1)
Cr–C(5)	2.138 (5)	2.147 (1)
Cr–C(6)	2.193 (5)	2.194 (2)
P(1)–C(7)	1.826 (5)	1.854 (1)
P(1)–C(8) C(12)	1.829 (5)	1.874 (1)
P(1)–C(9)	1.836 (4)	1.868 (1)
P(2)–C(15)	1.846 (5)	1.863 (1)
P(2)–C(16) C(18)	1.830 (6)	1.870 (1)
P(2)–C(17) C(8)	1.830 (4)	1.859 (1)
C(1)–C(2)	1.416 (7)	1.403 (2)
C(2)–C(3)	1.416 (7)	1.409 (2)
C(4)–C(5)	1.399 (7)	1.401 (2)
C(5)–C(6)	1.414 (7)	1.412 (2)
Bond Angles (deg)		
D(2)–Cr–D(1)	125.0	105.0
P(2)–Cr–P(1)	101.7 (1)	80.8 (1)
C(3)–C(2)–C(1)	120.2 (5)	120.6 (1)
C(6)–C(5)–C(4)	120.7 (5)	120.2 (1)

$CrCl_2$ with a donor ligand and an organolithium or -magnesium reagent. We report here the extension of this approach to the syntheses of η^3-allyl–Cr(II) compounds and discuss their reactions with alkynes and 1,3-dienes.

Results and Discussion

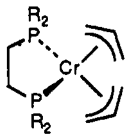
Preparation of $(\eta^3\text{-allyl})_2Cr(PR_3)_2$ and Related Compounds. $CrCl_2$, which may be prepared as a THF adduct by reacting $CrCl_3$ with Cr powder in THF, forms coordination complexes with P-donor ligands in which between one and four donor atoms are bonded to the metal atom. Stable $Cr(PR_3)_2Cl_2$ compounds can be prepared directly by reaction with PMe_2Ph[13] or PPh_2Me and are also present in the blue solutions formed upon reaction with PMe_3 or PEt_3. Attempted isolation, however, leads to ligand dissociation and formation of polymeric species of the type $[Cr(PR_3)Cl_2]_n$.[14] $Cr(PMe_3)_3Cl_2$ is the product of the reaction of $CrCl_3$ with magnesium in the presence of trimethylphosphine,[15] while $Cr(THF)Cl_2$ reacts with bidentate ligands to give $Cr(R_2PC_2H_4PR_2)_2Cl_2$ (R = Me)[11,12] or $[Cr(R_2PC_2H_4PR_2)Cl_2]_2$ (R = Pr^i).[16]

The $Cr(PR_3)_2Cl_2$ compounds are readily converted into Cr(II)–η^3-allyl species and the $(\eta^3\text{-}C_3H_5)_2Cr(PR_3)_2$ compounds 1–4 have been isolated from the reaction with 2-propenylmagnesium chloride or 2-methyl-2-propenylmagnesium chloride in diethyl ether at −78 °C (eq 1). The related compounds 5–7 are the products of the reactions involving $[Cr(Pr^i_2PC_2H_4PPr^i_2)Cl_2]_2$ and $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$.

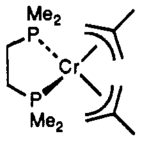


(1)

1: R = Me, R′ = H
2: R_3 = Me_2Ph, R′ = H
3: R_3 = Ph_2Me, R′ = H
4: R = Me, R′ = Me



5: R = Me
6: R = Pr^i



7

Compounds **1–7** are red, crystalline solids that are thermally unstable: **1** decomposes above −40 °C, **2**, **3**, and **6** decompose above −10 °C, and **5** and **7** decompose above ca. −20 °C. The only decomposition product that could be detected was a low yield of $(\eta^3\text{-}C_3H_5)_4Cr_2$. In addition to the compounds described above, $(\eta^3\text{-}C_3H_5)_2Cr(PEt_3)_2$ was prepared analogously but proved too unstable (decomposition at >−70 °C) to be isolated analytically pure while the reaction leading to **5** was accompanied by the formation of a golden yellow side product of unknown structure having a Cr:P ratio of ca. 1:5 and an absorption at 1475 cm^{-1} in the infrared spectrum.

The IR spectra of compounds **1–7** contain an absorption at ca. 1470 cm^{-1}, which is assigned to the η^3-allyl group. The crystal structure has been confirmed by X-ray diffraction studies of the most stable representatives **2** and **6**, which were undertaken mainly to determine the effect of the bidentate ligand upon the coordination at the metal atom. The molecular structures of the two compounds are shown in Figure 1, and selected structural parameters are listed in Table I. The structures of both compounds are very similar: the chromium atom lies in a distorted-tetrahedral environment defined by the midpoints of the allyl planes (D(1), D(2)) and two P atoms, the allyl groups are symmetrical, and the two planes form an angle of 25.7° (**2**) and 31° (**6**) to each other. The decrease in the D(1)–Cr–D(2) angle from 125.0° in **2** to 105.0° in **6** is probably the result of ring strain associated with the chelating ligand. Slight asymmetry in the bonding between the allylic groups and the Cr atom is observed in both compounds.

The reaction between $Cr(PMe_3)_2Cl_2$ and 2-butenylmagnesium chloride takes a different course: initially the reaction mixture has the orange-red color typical for an $(\eta^3\text{-allyl})_2Cr(PR_3)_2$ species but above −70 °C a color change to green occurs and a green oil could be isolated. The elemental analysis indicates that the oil has the expected composition ($C_{14}H_{32}CrP_2$), but treatment with HCl causes the liberation of 2,6-octadiene and 3-methyl-1,5-heptadiene, and not of butene, suggesting that reductive coupling of the two η^3-crotyl groups has occurred to give an η^2,η^2-bonded dimethyldiallyl group: head–head coupling giving the 2,6-octadiene species **8a** and head–tail coupling giving the 3-methyl-1,5-heptadiene species **8b** (eq 2). Reductive-coupling reactions of this nature have been reported for bis(η^3-allyl)Cr^{III} species.[1]

Reactions of the Bis(η^3-allyl)Cr^{II} Compounds with Alkynes and 1,3-Dienes. The reaction of bis(η^3-allyl)Cr^{III} compounds such as $Cp(\eta^3\text{-}C_3H_5)_2Cr$ with alkynes and 1,3-dienes is invariably accompanied by the reductive coupling of the allyl groups followed by displacement of the re-

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[11] Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

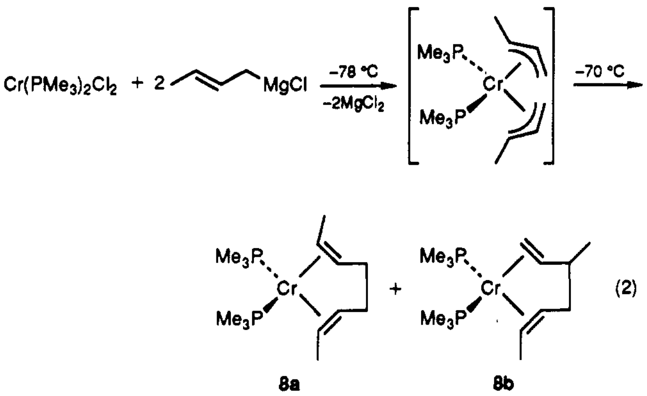
[12] Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

[13] Seidel, W.; Scholz, P. *Z. Chem.* **1978**, *18*, 149.

[14] Issleib, K.; Fröhlich, H. O. *Z. Anorg. Allg. Chem.* **1959**, *298*, 84.

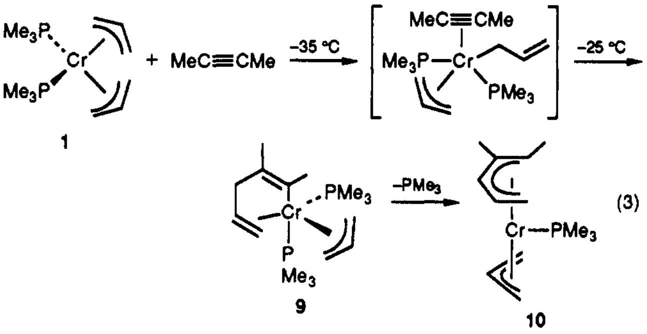
[15] Karsch, H. H. *Angew. Chem.* **1977**, *89*, 57.

[16] Hermes, A. R.; Girolami, G. S. *Inorg. Chem.* **1988**, *27*, 1775.



(2)

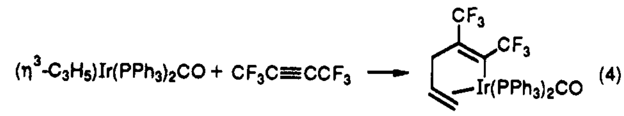
sulting 1,5-hexadiene from the metal atom.[1] In contrast, $(\eta^3\text{-}C_3H_5)_2Cr(PMe_3)_2$ (1) reacts with 2-butyne to give a green compound (9) whose IR spectrum indicates the presence of both an η^3-allyl group (υ 1450 cm^{-1}) and an uncomplexed double bond (υ 1645 cm^{-1}). GC analyses of the organic product of protolysis suggest that the compound contains a branched C_7 hydrocarbon. The compound is paramagnetic, and its structure has been established by the X-ray diffraction study discussed below, which confirms that a 2-butyne molecule has inserted into an η^3-allyl group to give an (η^1,η^2-4-methyl-1,4-hexadienyl)Cr^{II} species (eq 3). 9 reacts further above -25 °C with



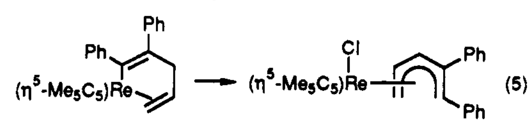
(3)

loss of PMe_3 to give a red-brown compound, which we provisionally assign as (η^5-1,2-dimethylpentadienyl)(η^3-C_3H_5)CrPMe$_3$ (10) by comparison with related compounds described in a following publication.[17]

The insertion of an alkyne into an η^3-allyl–Cr bond has not previously been reported, but a similar reaction has been observed between $(\eta^3\text{-}C_3H_5)Ir(PPh_3)_2CO$ and $CF_3C{\equiv}CCF_3$ (eq 4)[18] while a related species has been sug-



(4)



(5)

gested as an intermediate in the reaction between (η^5-Me_5C_5)(η^2-PhC≡CPh)ReCl$_2$ and 2-propenylmagnesium chloride, which, moreover, reacts further to give an (η^5-1,2-diphenylpentadienyl)Re species (eq 5).[19]

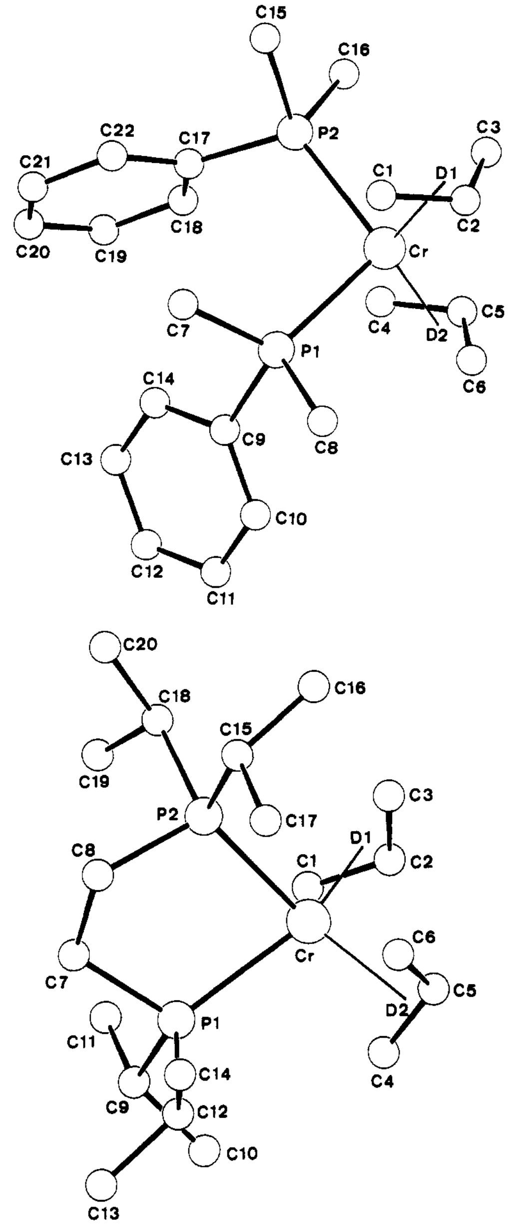


Figure 1. Molecular structures of (a, top) $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (2) and (b, bottom) $(\eta^3\text{-}C_3H_5)_2Cr(Pr^i{}_2PC_2H_4PPr^i{}_2)$ (6).

Table II. Selected Structral Parameters for $(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2$-4-methyl-1,4-hexadienyl)Cr(PMe$_3$)$_2$ (9)

	Bond Distances (Å)		
Cr–D(1)	1.963	Cr–C(14)	2.113 (5)
Cr–D(2)	2.024	C(7)–C(8)	1.396 (8)
Cr–P(1)	2.525 (2)	C(8)–C(9)	1.400 (8)
Cr–P(2)	2.398 (2)	C(10)–C(11)	1.435 (7)
Cr–C(7)	2.277 (6)	C(11)–C(12)	1.524 (7)
Cr–C(8)	2.200 (6)	C(12)–C(13)	1.497 (8)
Cr–C(9)	2.218 (5)	C(13)–C(14)	1.346 (7)
Cr–C(10)	2.147 (5)	C(13)–C(16)	1.522 (7)
Cr–C(11)	2.147 (5)	C(14)–C(15)	1.516 (8)
	Bond Angles (deg)		
D(2)–Cr–D(1)	136.1	C(14)–Cr–P(1)	170.8 (1)
D(2)–Cr–P(2)	104.3	C(9)–C(8)–C(7)	127.1 (5)
D(2)–Cr–P(1)	87.8	C(12)–C(11)–C(10)	118.5 (4)
D(1)–Cr–P(2)	119.5 (1)	C(13)–C(12)–C(11)	110.6 (4)
D(1)–Cr–P(1)	91.2 (1)	C(14)–C(13)–C(12)	119.3 (4)
C(14)–Cr–P(2)	88.5 (1)	C(13)–C(14)–Cr	116.0 (4)

The crystal structure of 9 has been established by X-ray diffraction (Figure 2) and selected structural parameters are listed in Table II. The metal atom lies at the center of a distorted trigonal bipyramid with one of the phosphine ligands and the η^1-bonded C atom of the organyl chain in

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[17] Jolly, P. W.; Krüger, C.; Zakrzewski, U. *J. Organomet. Chem.*, in press.

[18] Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1142.

[19] Fischer, R. A.; Herrmann, W. A. *J. Organomet. Chem.* **1989**, *377*, 275.

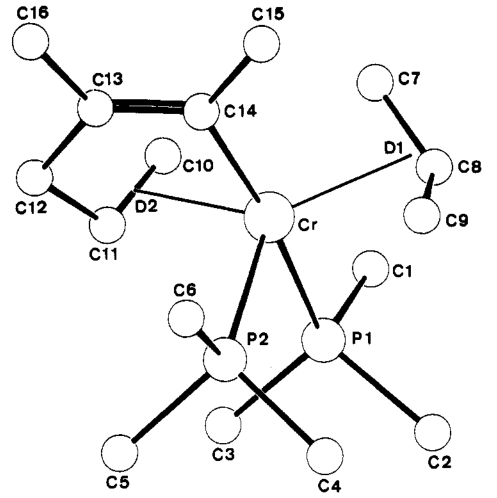
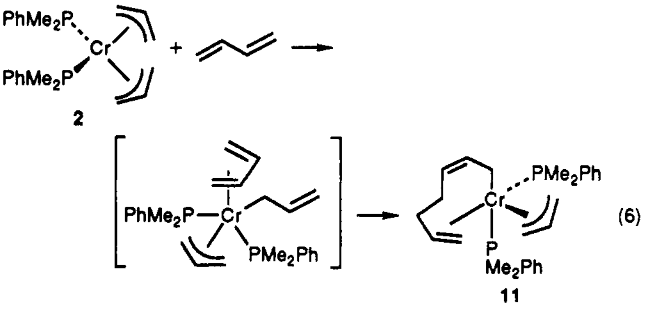


Figure 2. Molecular structure of (η^3-C_3H_5)(η^1,η^2-4-methyl-1,4-hexadienyl)Cr(PMe_3)$_2$ (**9**).

the axial positions. The second phosphine ligand, the midpoints of the complexed double bond (D(2)), and the center of the allyl plane (D(1)) occupy the equatorial positions. The atoms C(11)–C(14) of the organyl chain are essentially coplanar. The Cr–P distances are markedly different, while the Cr–C(14) distance is typical for a σ-bond between the metal atom and an sp^2-hybridized C atom.

The reaction of **1** with acetylene, 1-butyne, 3-hexyne, or 4-octyne at low temperatures also led to the formation of red solutions; however, we were unable to isolate any well-defined products. Interestingly, complexes **5**–**7**, which contain chelating ligands, do not react with alkynes.

The (η^3-allyl)$_2$Cr(PR_3)$_2$ compounds **1**–**4** (but not compounds **5**–**7**) also react with 1,3-dienes. For example, (η^3-C_3H_5)$_2$Cr(PMe_2Ph)$_2$ (**2**) reacts with 1,3-butadiene at −30 °C to give a green product that melts at ca. −60 °C and whose analytical data suggest that a diene molecule has inserted into an allyl group to give a compound (**11**) provisionally suggested to contain an η^1,η^2-1,5-heptadienyl group (eq 6). GC analysis (after hydrogenation) of the protolysis products indicates that the compound contains a linear, unsaturated C_7 hydrocarbon, while the IR spectrum suggests the presence of an uncomplexed double bond (υ 1630 cm^{-1}). Isoprene, 1,3-hexadiene, and 2,3-dimethylbutadiene behave similarly, but no reaction is observed with 2,4-hexadiene or cyclic dienes.



Preparation of R$_2$Cr(PR$_3$)$_2$ Compounds. It is convenient to mention here our experience with the preparation of bis(alkyl)–Cr^{II} species. The first $Ar_2Cr(PR_3)_2$ compounds were reported in 1974,[9] and the square-planar geometry was confirmed by X-ray diffraction of a PMe_3-stabilized example.[10] In contrast, it has been reported that the reaction of Cr(PMe_2Ph)$_2Cl_2$ with MeLi does not lead to the expected Me_2Cr^{II} species.[13]

In our hands, Cr(PMe_3)$_2Cl_2$ reacts with MeLi at −78 °C to give an orange-yellow crystalline complex that decomposes above −60 °C. Although facile PMe_3 dissociation made it impossible to obtain satisfactory analytical data, the detection of methane (85% theory, MS) upon protolysis supports the formulation as $Me_2Cr(PMe_3)_2$. A similar reaction is observed between Cr(PMe_3)$_2Cl_2$ and EtMgCl: a dark red compound is formed, which decomposes above −60 °C and which we assume to be $Et_2Cr(PMe_3)_2$. Although attempted controlled decomposition of this compound in a vessel attached to a gas buret led to an explosion, it did prove possible to confirm qualitatively the liberation of ethane. Finally, the product of the reaction between Cr($Me_2PC_2H_4PMe_2$)$_2Cl_2$ and EtMgCl is a red, crystalline species whose analytical data and the observation of broad signals in the ^{1}H NMR spectrum suggest that it is the paramagnetic species $Et_2Cr(Me_2PC_2H_4PMe_2)_2$ (and not a diamagnetic 18-electron compound containing an agostic ethyl group) related to the analogous Me_2Cr^{II} species isolated earlier.[11]

None of the compounds mentioned above react with alkynes or dienes.

Experimental Section

Most of the compounds described below are thermally labile and sensitive to air and moisture, and all experiments were carried out at low temperatures and under argon. Diethyl ether, THF, toluene, and pentane were dried and freed from dissolved oxygen by distillation from diethylmagnesium. Hexane was dried by distillation from $CaCl_2$. Infrared spectra were recorded as KBr disks with a Nicolet 7199 FT spectrometer. Elemental analyses were performed by the microanalytical laboratories of Dornis and Kolbe, Mülheim a.d. Ruhr. Cr(PMe_3)$_2Cl_2$,[15] Cr(PEt_3)$_2Cl_2$,[14] Cr(PMe_2Ph)$_2Cl_2$,[13] Cr($Me_2PC_2H_4PMe_2$)$_2Cl_2$,[11,12] and [Cr($Pr^i_2PC_2H_4Pr^i_2$)Cl_2]$_2$[16] were prepared by published procedures.

Cr(THF)Cl$_2$. A suspension of anhydrous $CrCl_3$ (249 g, 1.57 mol) and Cr powder (44 g, 0.846 mol) in THF (2 L) was heated under reflux for 1 week, during which period a color change from violet to pale green occurred. The reaction mixture was filtered and the pale green product separated from excess Cr powder by Soxhlet extraction with THF. The product was washed with pentane (5 × 100 mL) and dried in vacuo. Yield: 370 g (1.9 mol, 81%). Depending upon the drying conditions, compounds can be obtained which have the composition Cr(THF)$_2Cl_2$ (pale green), Cr(THF)Cl_2, (bright blue) or $CrCl_2$ (gray). Cr(THF)Cl_2 was used in the following reactions.

Cr(PPh$_2$Me)$_2$Cl$_2$. Cr(THF)Cl_2 (2.0 g, 10.3 mmol) was suspended in toluene, and PPh_2Me (3.9 mL, 21.0 mmol) was added slowly. The reaction mixture was heated at 80 °C for 2 h to give a blue suspension. Solvent was removed in vacuo and the residue washed with pentane (2 × 10 mL). Yield: 5.1 g (9.7 mmol, 95%). Anal. Calcd for $C_{26}H_{26}CrCl_2P_2$: C, 59.7; H, 5.0; Cl, 13.6; Cr, 9.9; P, 11.8. Found: C, 60.0; H, 5.1; Cl, 13.3; Cr, 9.6; P, 11.6. IR (KBr): 1430 (s) cm^{-1}.

(η^3-C$_3$H$_5$)$_2$Cr(PMe$_3$)$_2$ (1). A solution of Cr(PMe_3)$_2Cl_2$ was prepared from Cr(THF)Cl_2 (8.0 g, 41.0 mmol) and PMe_3 (8.8 mL, 85 mmol) in diethyl ether (200 mL) and cooled to −78 °C. Ethereal 2-propenylmagnesium chloride (213 mL of a 0.4 M solution, 85 mmol) was added slowly, the color of the reaction mixture changing from blue to orange. The reaction mixture was stirred for 12 h at −30 °C and filtered, and the solvent was removed in vacuo at −30 °C. The orange residue was extracted with precooled pentane and the extract cooled to −78 °C to give the compound as red needles, which were isolated, washed with precooled pentane at −78 °C, and dried in vacuo. Yield: 8.0 g (28.0 mmol, 68%). Anal. Calcd for $C_{12}H_{28}CrP_2$: C, 50.3; H, 9.9; Cr, 18.2; P, 21.6. Found: C, 50.1; H, 10.2; Cr, 18.0; P, 21.5. IR (KBr): 3030 (m), 1470 (m), 1420 (s), 1275 (s), 1195 (m), 940 (s) cm^{-1}.

(η^3-C$_3$H$_5$)$_2$Cr(PMe$_2$Ph)$_2$ (2). Prepared as above (60% yield) as a red, crystalline solid from Cr(THF)Cl_2, PMe_2Ph, and 2-propenylmagnesium chloride in diethyl ether. Anal. Calcd for $C_{22}H_{32}CrP_2$: C, 64.4; H, 7.9; Cr, 12.7; P. 15.1. Found: C, 63.1; H, 8.3; Cr, 13.1; P, 15.5. Crystal structure: see text.

(η^3-C$_3$H$_5$)$_2$Cr(PPh$_2$Me)$_2$ (3). Prepared as above (63% yield) as an orange-red, crystalline solid from Cr(THF)Cl_2, PPh_2Me, and

Table III. Crystallographic Data for $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (2), $(\eta^3\text{-}C_3H_5)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$ (6), and $(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2\text{-}4\text{-methyl-1,4-hexadienyl})Cr(PMe_3)_2$ (9)

	2	6	9
formula	$C_{22}H_{32}CrP_2$	$C_{20}H_{42}CrP_2$	$C_{16}H_{34}CrP_2$
mol wt, g/mol	410.4	396.5	340.4
a, Å	8.894 (4)	9.171 (1)	9.299 (5)
b, Å	27.56 (1)	15.936 (2)	14.474 (8)
c, Å	9.355 (3)	15.368 (1)	13.916 (5)
α, deg	90.0	90.0	90.0
β, deg	107.64 (3)	102.22 (1)	90.0
γ, deg	90.0	90.0	90.0
cryst size, mm	0.18 × 0.36 × 0.47	0.32 × 0.54 × 0.36	0.29 × 0.36 × 0.40
V, Å^3	2185.1	2195.0	1872.9
T, °C	−173	−173	−173
D_c, g cm^{-3}	1.25	1.20	1.21
λ(Mo), Å	0.71069	0.71069	0.71069
Z	4	4	4
space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_12_12_1$ (19)
data collcd	±*h*,+*k*,+*l*	±*h*,+*k*,+*l*	±*h*,+*k*,+*l*
reflns measd	5365	5365	4589
ind reflns	4962	4995	4238
obsd reflns	3971	4500	3351
no. of variables	354	376	172
R	0.050	0.025	0.059
R_w	0.076	0.031	0.051
res electron density (near Cr), e Å^{-3}	0.76	0.36	1.10
enantiomorph polarity parameter (χ)			0.03[20]

2-propenylmagnesium chloride in diethyl ether. Anal. Calcd for $C_{32}H_{36}CrP_2$: C, 71.9; H, 6.8; Cr, 9.7; P, 11.6. Found: C, 72.1; H, 7.1; Cr, 9.4; P, 11.3. IR (KBr): 3050 (m), 1430 (s), 1180 (m), 880 (s) cm^{-1}.

$(\eta^3\text{-}C_3H_5)_2Cr(Me_2PC_2H_4PMe_2)$ (5). Prepared as above (29% yield) as red needles from $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$ and 2-propenylmagnesium chloride in diethyl ether. Anal. Calcd for $C_{12}H_{26}CrP_2$: C, 50.7; H, 9.2; Cr, 18.3; P, 21.8. Found: C, 50.6; H, 9.2; Cr, 18.4; P, 21.7. IR (KBr): 3035 (m), 1470 (m), 1420 (s), 1275 (s), 1200 (m), 935 (s) cm^{-1}.

$(\eta^3\text{-}2\text{-}MeC_3H_4)_2Cr(PMe_3)_2$ (4). Prepared as described above (55% yield) as a red, crystalline solid from $Cr(THF)Cl_2$, PMe_3, and 2-methyl-2-propenylmagnesium chloride in diethyl ether. Anal. Calcd for $C_{14}H_{32}CrP_2$: C, 53.5; H, 10.3; Cr, 16.5; P, 19.7. Found: C, 53.6; H, 10.1; Cr, 16.7; P, 19.7. IR (KBr, −45 °C): 3030 (m), 1460 (m), 1420 (s), 1360 (m), 940 (s) cm^{-1}.

$(\eta^3\text{-}2\text{-}MeC_3H_4)_2Cr(Me_2PC_2H_4PMe_2)$ (7). Prepared as described above (52% yield) as a red, crystalline solid from $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$ and 2-methyl-2-propenylmagnesium chloride in diethyl ether. Anal. Calcd for $C_{14}H_{30}CrP_2$: C, 53.8; H, 9.7: Cr, 16.7; P, 19.8. Found: C, 52.4; H, 9.5; Cr, 17.3; P, 21.0 (the compound contains an impurity having a high P content; see text). IR (KBr, −45 °C): 3035 (m), 1470 (m), 1410 (s), 1360 (m), 1265 (s), 935 (s) cm^{-1}.

$(\eta^3\text{-}C_3H_5)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$ (6). $Cr(THF)Cl_2$ (1.95 g, 10.0 mmol) was suspended in toluene (50 mL) at room temperature, $Pr^i_2PC_2H_4PPr^i_2$ (2.62 g, 10.0 mmol) was added, and the reaction mixture was stirred at 60 °C for 1 h. The solvent was removed in vacuo and the resulting blue powder suspended in diethyl ether and treated with ethereal 2-propenylmagnesium chloride (51.3 mL of a 0.4 M solution, 20.5 mmol) as described above. The compound was isolated as dark red crystals. Yield: 2.2 g (5.5 mmol, 55%). Anal. Calcd for $C_{20}H_{42}CrP_2$: C, 60.6; H, 10.7; Cr, 13.1; P, 15.6. Found: C, 60.1; H, 11.1; Cr, 13.1; P, 15.6. IR (KBr): 3035 (m), 1205 (m) cm^{-1}. Crystal structure: see text.

$(\eta^2,\eta^2\text{-dimethyldiallyl})Cr(PMe_3)_2$ (8a/b). $Cr(THF)Cl_2$ (1.0 g, 5.1 mmol) and PMe_3 (1.1 mL, 10.5 mmol) were dissolved in diethyl ether (40 mL), the solution was cooled to −78 °C, and an ethereal solution of 2-butenylmagnesium chloride (44.4 mL of a 0.24 Mol solution, 10.5 mmol) was added slowly. The color of the reaction mixture changed from blue to orange. The mixture was warmed to −35 °C and stirred for 12 h. The resulting green solution was filtered at −30 °C and evaporated to dryness in vacuo and the green residue extracted with precooled hexane. Evaporation of the extract gave the compound as a green oil. Yield: 0.94 g (59% theory). Anal. Calcd for $C_{14}H_{32}CrP_2$: C, 53.5, H, 10.3; Cr, 16.5; P, 19.7. Found: C, 51.6; H, 10.1; Cr, 16.8; P, 19.7. IR (KBr): 3040 (m), 1450 (m), 1420 (m), 1280 (s), 935 (s) cm^{-1}. Treatment with HCl and GC analysis of the organic product showed the presence of 3-methyl-1,5-heptadiene (43.4%) and 2,6-octadiene (28.7%).

$(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2\text{-}4\text{-methyl-1,4-hexadienyl})Cr(PMe_3)_2$ (9). A solution of $(\eta^3\text{-}C_3H_5)_2Cr(PMe_3)_2$ (1) was prepared as described above from $Cr(THF)Cl_2$ (1.47 g, 7.5 mmol), PMe_3 (1.6 mL, 15.5 mmol), and 2-propenylmagnesium chloride (37 mL of a 0.42 M solution, 15.5 mmol) in diethyl ether at −78 °C and stirred at −30 °C for 2 h. 2-Butyne (5 mL, 64 mmol) was added and the reaction mixture stirred at −30 °C for 12 h, during which time a color change from orange to green occurred. The solvent was removed in vacuo at −30 °C and the residue washed with pentane (2 × 10 mL) at −78 °C and then extracted with pentane at −30 °C. The extract was cooled to −78 °C to give the compound as green crystals. Yield: 1.02 g (3.0 mmol, 40%). Anal. Calcd for $C_{16}H_{34}CrP_2$: C, 56.5; H, 10.1; Cr, 15.3; P, 18.2. Found: C, 56.2; H, 10.1; Cr, 15.0; P, 16.1 (rapid decomposition at −25 °C with loss of PMe_3 made it difficult to obtain satisfactory analytical data). IR (KBr, −70 °C): 3030 (m), 1645 (m), 1450 (m), 1420 (s), 1380 (m), 1280 (s), 960 (s) cm^{-1}. Crystal structure: see text.

Reaction of $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (2) with 1,3-Butadiene. 2 (2.8 g, 6.0 mmol) was suspended in diethyl ether, and 1,3-butadiene (0.6 mL, 7 mmol) was added at −30 °C. The green solution was stirred for 12 h, solvent was removed in vacuo at −30 °C, and the resulting oil was dissolved in hexane at −30 °C. Cooling the hexane solution to −78 °C gave a green solid tentatively identified as $(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2\text{-}1,5\text{-heptadienyl})Cr(PMe_3)_2$ (11), which melted at ca. −60 °C. Yield: 1.6 g (3.4 mmol, 57%). Anal. Calcd for $C_{26}H_{38}CrP_2$: C, 67.2; H, 8.2; Cr, 11.2; P, 13.3. Found: C, 67.2, H. 7.3; Cr, 11.5; P, 13.9. IR (KBr): 1630 (m), 1430 (s), 1290 (s) 940 (s) cm^{-1}. Protolysis with HCl followed by hydrogenation led to the elimination of *n*-heptane (65%, GC/MS).

$Me_2Cr(PMe_3)_2$. A solution of $Cr(PMe_3)_2Cl_2$, prepared from $Cr(THF)Cl_2$ (2.0 g, 10.3 mmol) and PMe_3 (2.1 mL, 20.6 mmol), was prepared in diethyl ether (40 mL), cooled to −78 °C, and treated with an ethereal solution of MeLi (11.7 mL of a 1.8 M solution, 21 mmol). The color of the reaction mixture changed from blue to orange. The reaction mixture was stirred at −30 °C for 12 h, filtered, and evaporated to dryness in vacuo. The orange-yellow residue was extracted with precooled pentane at −30 °C and the extract cooled to −78 °C to give the compound as orange cubes, which were dried for 20 min at −78 °C. Yield: 1.47 g (61% theory). Anal.: attempts to weigh samples for analysis were accompanied by decomposition. IR (KBr, −70 °C): 1425 (s), 1120 (m), 940 (s) cm^{-1}. Protolysis with H_2SO_4 led to the evolution of methane (87% theory, MS) as well as hydrogen and traces of ethylene and ethane.

$Et_2Cr(Me_2PC_2H_4PMe_2)_2$. A suspension of Cr-

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$(Me_2PC_2H_4PMe_2)_2Cl_2$ (1.0 g, 2.4 mmol) in diethyl ether (30 mL) was cooled to −78 °C and treated with an ethereal solution of EtMgCl (11.7 mL of a 0.41 M solution, 4.8 mmol). The reaction mixture was warmed to −30 °C, stirred for 12 h, filtered at −30 °C, and evaporated to dryness in vacuo. The orange residue was extracted with precooled pentane at −30 °C and the extract cooled to −78 °C to give the compound as red crystals, which were dried at −30 °C. Yield: 0.77 g (78% theory). Anal. Calcd for $C_{16}H_{42}CrP_4$: C, 46.8; H, 10.3; Cr, 12.7; P, 30.2. Found: C, 46.9; H, 10.3; Cr, 12.5; P, 30.3. IR (KBr, −50 °C): 1455 (m), 1420 (s), 1350 (m), 935 (s), 920 (s) cm^{-1}.

Single-Crystal X-ray Diffraction Studies of 2, 6, and 9. The crystal structure analyses were carried out with an Enraf-Nonius CAD-4 diffractometer. Crystallographic data and details of the refinement are listed in Table III and in the supplementary material.

Registry No. 1, 135943-57-6; 2, 135943-58-7; 3, 135943-59-8; 4, 135943-60-1; 5, 135943-61-2; 6, 135943-62-3; 7, 135943-63-4; 8a, 135943-64-5; 8b, 135943-65-6; 9a, 135972-33-7; 10, 135943-66-7; 11, 135943-67-8; $Me_2Cr(PMe_3)_2$, 135943-68-9; $Et_2Cr(Me_2PC_2H_4PMe_2)_2$, 135943-69-0; $Cr(THF)Cl_2$, 36463-97-5; $Cr(PPh_2Me)_2Cl_2$, 135943-70-3; $CrCl_3$, 10025-73-7; $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$, 135943-71-4; $Cr(PMe_3)_2Cl_2$, 135943-72-5; 2-propenylmagnesium chloride, 2622-05-1; 2-methyl-2-propenylmagnesium chloride, 5674-01-1; 2-butenylmagnesium chloride, 6088-88-6; 1,3-butadiene, 106-99-0; 2-butyne, 503-17-3.

Supplementary Material Available: Detailed information on the crystal structure determination of 2, 6, and 9 including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles (17 pages); lists of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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(20) Flack, H. D. *Acta Crystallogr.* 1983, *A39*, 876. The handedness is that shown in Figure 2.

Formation of Carbon–Carbon Bonds by Oxidative-Addition Reactions to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$

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Oxidative addition of various organic halides to *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ has been examined by variable-temperature NMR spectroscopy. For $PhCH_2Cl$, $CH_3C(O)Cl$, $Ph_2CHC(O)Cl$, PhC(O)Cl, and $PhCH_2C(O)Cl$ oxidative addition is followed by reductive elimination to form carbon–carbon bonds. For reaction of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ with $CH_3C(O)Cl$ the intermediate is characterized by ^1H and ^{31}P NMR spectroscopy at −5°; acetone elimination is significant at 10 °C. For the other complexes the oxidative addition is sufficiently slow that an intermediate cannot be identified. Oxidative addition of MeI and EtI to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ leads to complexes Ir(CO)(I)(R)(Me)(P(*p*-tolyl)$_3$)$_2$ that are characterized by ^1H and ^{31}P NMR spectroscopy. For R = Me this complex is stable; for R = Et the complex slowly undergoes β-elimination leading to C_2H_4 and CH_4. These results provide strong support for a mechanism involving halide dissociation from the iridium(III) complexes.

Formation of carbon–carbon bonds is a major focus for organic and organometallic chemists. Catalytic systems involving transition-metal complexes most often form a carbon–carbon bond through alkyl → acyl conversions with carbon monoxide.[1] However, there exist increasing examples of carbon–carbon bond formation through reductive-elimination reactions.

A theoretical study of C–C bond formation on palladium and platinum centers attributes the less facile formation of C–C bonds in comparison to C–H bonds to the directionality of the sp^3 hybrids.[2] Thus, bond formation between two sp^3 centers should be a higher energy process than between an sp^3 center and an sp^2 center or to an atom that only uses s orbitals. These studies also show that reductive elimination is favored by palladium over platinum and by M(IV) over M(II).[2] A theorectial study on the possible geometrical preferences of $Ni(L)_3(R)_2$ formed in the associative path for reductive elimination from $Ni(L)_2(R)_2$ has also been reported.[3]

Stille and co-workers reported on the reductive elimination of ethane from dimethylpalladium complexes.[4] These studies showed that the reductive elimination required a cis orientation of methyls, proceed with retention of configuration at the carbon, and were inhibited by excess phosphine ligand.[4]

Reductive-elimination reactions on palladium centers have continued to attract attention.[5] Reductive elimination of ethane from $Pd(Me)_3(bpy)I$ apparently involves dissociation of I^- prior to the reductive elimination.[5] Addition of allyl bromide to $PdMe_2$(tripod) (tripod = a tridentate nitrogen-donor ligand) led to ethane and the η^3-allyl product.[6] Cross-coupling of C_6H_5I and MeMgI catalyzed by *trans*-Pd(Ph)(I)$(PEt_2Ph)_2$ led to toluene with a selectivity of over 90%, apparently through a reductive-elimination reaction.[7] Coupling of an allyl and phenyl

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(1) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Masters, C. *Homogeneous Transition Metal Catalysis*; Chapman and Hall: London, 1981. (c) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Mill Valley, CA, 1985.

(2) (a) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* 1986, *108*, 6115. (b) Low, J. J.; Goddard, W. A., III. *Organometallics* 1986, *5*, 609.

(3) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, T. *J. Am. Chem. Soc.* 1984, *106*, 8181.

(4) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* 1980, *102*, 4933. (b) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* 1981, *103*, 4174.

(5) Byers, P. K.; Canty, Z. J.; Crespo, M.; Puddephatt, P. J.; Scott, J. D. *Organometallics* 1988, *7*, 1363.

(6) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* 1990, *9*, 1231.

(7) Ozawa, F.; Kurihara, K.; Fugimore, M.; Hidaka, T.; Toyoshima, J.; Yamamoto, A. *Organometallics* 1989, *8*, 180.

0276-7333/91/2310-3525$02.50/0