collected at room temperature, and the individual profiles have been analyzed following Lehmann and Larsen.[39] Intensities were corrected for Lorentz and polarization effects. No correction for absorption was necessary.

All structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms (**5b** and **6**), for all non-hydrogen atoms except the carbon atoms of the phenyl rings (**7d**), for all non-hydrogen atoms except the carbon and oxygen atoms of the methoxymethyl substituent (which was found disordered and distributed in two positions of equal occupancy factors) and the atoms of the tetrahydrofuran of solvation (which were treated all as carbon atoms) (**8d**), and for only the Mn and P atoms (**4c**). All the hydrogen atoms of **6** and **7d** were clearly located in the final ΔF map and refined isotropically; those of **4c**, **5b** (except the hydride, clearly located), and **8d** (except those of the disordered methoxymethyl substituent and of the solvent molecule) were placed at their geometrically calculated positions and refined "riding" the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 40. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[41] The final atomic coordinates for the non-hydrogen atoms are given in Tables V (**4c**), VI (**5b**), VII (**6**), VIII (**7d**), and IX (**8d**).

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Registry No. 1, 116405-31-3; **2**, 37523-60-7; **3a**, 116405-35-7; **3b**, 137394-40-2; **4b**, 137433-72-8; **4c**, 137433-71-7; **4d**, 137433-73-9; **5a**, 137394-43-5; **5b**, 137394-46-8; **5c**, 137394-41-3; **5d**, 137394-50-4; **6d**, 137394-42-4; **7a**, 137394-44-6; **7d**, 137394-47-9; **8a**, 137394-45-7; **8d**, 137394-49-1; $[Mn_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)(CO)_6]$, 137394-39-9; *fac*-$[Mn(C_2Ph)(CO)_3(dppm)]$, 103902-92-7; *fac*-$[Mn(H)(CO)_3(dppm)]$, 36344-24-8; $[Mn_2(CO)_6(dppm)_2]$, 57403-90-4; $[Mn_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$, 56665-73-7; HC_2Ph, 536-74-3; $HC_2{}^tBu$, 917-92-0; HC_2CO_2Me, 922-67-8; HC_2CH_2OMe, 627-41-8; acetylene, 74-86-2.

Supplementary Material Available: Listings of hydrogen coordinates and thermal parameters (Tables SI–SV), thermal parameters (Tables SVI–SX), and bond distances and angles (Tables XI–XV) (32 pages); listings of observed and calculated structure factors (77 pages). Ordering information is given on any current masthead page.

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(39) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* 1974, *30*, 580.

(40) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

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Metal-Induced 1,5- and 1,4-Hydrogen Shifts in Polysubstituted Butadienyl Units η^3-Bonded to Palladium[†]

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3-Hexyne (2 equiv) is readily inserted into the Pd–C bond of the cyclopalladated compound derived from the ((dimethylamino)methyl)ferrocene ligand, affording a kinetic isomer, 2. The latter may be isomerized into a thermodynamic isomer 3 in pyridine at 100 °C. Two further isomers of 2 are produced in refluxing pyridine and with maleic anhydride in refluxing toluene. The former is the result of a 1,4-H shift of the CH_2 group γ to the palladium atom on the butadienyl chain whereas the latter is obtained via a 1,5-H shift of the CH_2 unit δ to the palladium.

Introduction

The synthesis of butadienyl fragments η^3-bound to a palladium center may be achieved via insertion of two alkynes into Pd–X bonds[1] (X = Cl, Ph) or into the Pd–C bond of cyclopalladated compounds. Several structure determinations[2-5] have shown that the butadienyl units formed invariably display the same features. Each contains one C–C double bond η^2-bound at the palladium atom and a second η^1-bound olefin moiety. This bonding mode is obviously reminiscent of that of allylic fragments. However, in contrast to allylic units whose chemistry has been extensively investigated and which are still part of

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[†] Reactivity of cyclopalladated compounds part 27. For part 26, see ref 8.

(1) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161.

(2) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S. E.; LeBorgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547. Albert, J.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1989**, *379*, 177. Ricci, J. S.; Ibers, J. A. *J. Organomet. Chem.* **1971**, *27*, 261.

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(4) Dupont, J.; Pfeffer, M.; Daran, J. C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421.

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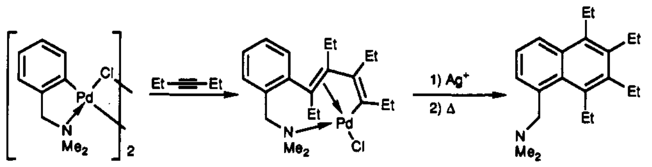
0276-7333/92/2311-0386$03.00/0

important research programs,[6] so far very few reactivity studies have been reported on organometallic compounds containing butadienyl moieties.[3] Nevertheless, it was shown that depalladation of butadienyl complexes may lead to several rearrangements of the remaining organic fragments.[7] The nature of the resulting organic compounds is dependent both on the cyclopalladated amine and on the alkyne substituents present. Notably, it was found that heterocycles could be synthesized via nucleophilic addition of the nitrogen atom of the palladated ligand to the olefin unit activated through its η^2-interaction with Pd.[8-10] Furthermore, several side reactions were found to occur such as annulation of phenyl groups or dealkylation of esters leading respectively to naphthyl, fulvene,[3,5,11] or pyrone units.[12]

We now present further studies of the chemistry of these compounds in order to evaluate their synthetic potential. In this paper, we present the reactivity of a compound in which the alkyne substituents are all ethyl groups. It was shown recently that under depalladation conditions, a novel annulation reaction could be observed with the palladated dimethylbenzylamine ligand[3] (eq 1). Here we have investigated the reactivity displayed by another cyclopalladated ligand (((dimethylamino)methyl)ferrocene) and observed different behavior. In contrast to the previous study (eq 1), we have not seen annulation of cyclopentadienyl, although such a reaction should be feasible in view of the well-established analogy between the chemical reactivity of an aryl and that of a cyclopentadienyl ring of a ferrocene unit.



(1)

Results and Discussion

The synthesis of the starting compound 2 through the addition of 3-hexyne to 1 has been described independently by us[5] and Heck et al.[3] Its X-ray molecular structure[3] revealed no unusual features when compared to similar compounds.[2,4,5]

Attempts were made to depalladate 2 by treating it first with a silver salt and then by heating the resulting cationic complex to ca. 130 °C (i.e. the conditions used in eq 1). This procedure proved unsatisfactory and resulted in complete decomposition. However, it was shown in our group[12] that depalladation of organopalladium compounds could also be efficiently achieved, to afford annulation

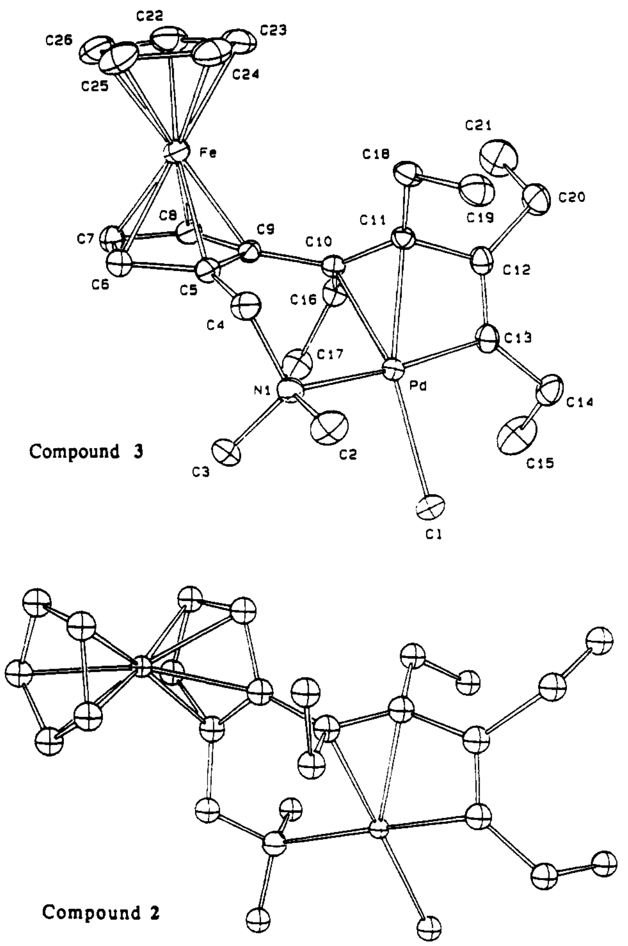


Figure 1. ORTEP view of compound 3 together with that of 2 (taken from ref 3) showing the conformational changes on going from 2 to 3.

Table I. Positional Parameters and Their Esd's for 3

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pd	0.73880 (2)	0.15500 (1)	0.31449 (2)	2.602 (3)
Fe	0.90335 (5)	0.12233 (2)	−0.12356 (4)	3.558 (9)
Cl	0.6971 (1)	0.21017 (3)	0.47676 (8)	4.51 (2)
N1	0.9175 (3)	0.20411 (8)	0.2499 (2)	3.19 (5)
C2	1.0344 (4)	0.2136 (1)	0.3655 (4)	4.77 (8)
C3	0.8499 (5)	0.2506 (1)	0.2002 (3)	4.57 (8)
C4	0.9990 (3)	0.1812 (1)	0.1478 (3)	3.62 (6)
C5	0.8926 (4)	0.1708 (1)	0.0262 (3)	3.21 (6)
C6	0.8979 (4)	0.1946 (1)	−0.0963 (3)	4.26 (7)
C7	0.7709 (4)	0.1798 (1)	−0.1852 (3)	4.54 (7)
C8	0.6853 (4)	0.1472 (1)	−0.1198 (3)	3.73 (6)
C9	0.7565 (3)	0.1414 (1)	0.0131 (3)	2.82 (5)
C10	0.6810 (3)	0.1174 (1)	0.1191 (3)	2.79 (5)
C11	0.7538 (3)	0.0854 (1)	0.2130 (3)	2.98 (5)
C12	0.6608 (4)	0.0658 (1)	0.3144 (3)	3.66 (6)
C13	0.6204 (4)	0.1024 (1)	0.3851 (3)	3.63 (6)
C14	0.5287 (5)	0.1043 (1)	0.4988 (3)	5.23 (8)
C15	0.3783 (5)	0.1310 (2)	0.4663 (5)	7.7 (1)
C16	0.5043 (4)	0.1200 (1)	0.0895 (3)	3.85 (7)
C17	0.4358 (4)	0.1703 (2)	0.0845 (4)	5.37 (9)
C18	0.9103 (4)	0.0636 (1)	0.2101 (3)	3.75 (6)
C19	1.0107 (4)	0.0611 (1)	0.3424 (4)	5.05 (8)
C20	0.6318 (5)	0.0128 (1)	0.3252 (4)	5.94 (9)
C21	0.5384 (7)	−0.0077 (2)	0.2048 (5)	8.8 (1)
C22	0.8886 (5)	0.0658 (1)	−0.2505 (4)	5.74 (9)
C23	0.9497 (5)	0.0508 (1)	−0.1238 (4)	5.07 (8)
C24	1.0865 (4)	0.0764 (2)	−0.0867 (4)	5.55 (9)
C25	1.1086 (5)	0.1079 (2)	−0.1899 (4)	6.5 (1)
C26	0.9846 (5)	0.1008 (2)	−0.2909 (4)	6.5 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

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(6) See for example: Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 8, pp 799–938. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. Trost, B. M.; Verhoeven, T. R. *Ibid.* **1980**, *102*, 4743. Åkermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275. Kurosawa, H.; Emoto, M.; Ohnishi, H,; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333.

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(9) Pfeffer, M.; Rotteveel, M. A. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 317.

(10) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *Organometallics* **1987**, *6*, 2029.

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(12) Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J.; Le Borgne, G. *J. Organomet. Chem.* **1991**, *413*, C15.

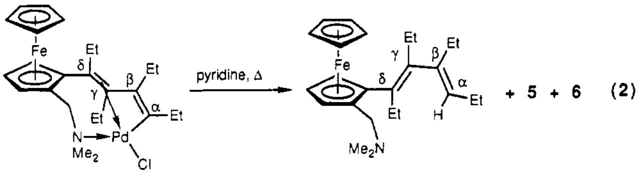
reactions of aryl rings, by treatment with neat pyridine at reflux temperature.

We found that heating **2** in pyridine at 100 °C resulted in a gradual change in the color of the solution from orange to orange-red. If the reaction mixture is subjected to prolonged heating, metallic palladium separates from the reaction mixture (vide infra). Analysis of the red solution showed the presence of a new compound **3** together with unchanged **2**, the ratio of **3**:**2** being 1:1. Compound **3** has the same analytical composition as **2**; however its ^{1}H NMR spectrum showed dramatic changes when compared to that of **2**. Whilst all of the four ethyl groups are still present, the CH_2 protons of the (dimethylamino)methyl unit appear at very different chemical shifts. Moreover, one methylene proton of an ethyl group resonates at a rather low field shift (3.82 vs 2.0–2.4 ppm).

The structure of **3** has been determined by an X-ray diffraction study. An ORTEP diagram of the molecule is shown in Figure 1. It is immediately apparent from this study that the structure of **3** can be produced from that of **2** by inverting the configuration of either the ferrocene moiety or the nine-membered palladocyclic ring. Indeed, in **2** and **3** two different types of planar chirality are present and thus **2** and **3** are two diastereomers. It is possible to envisage the configurational change of the molecule on going from **3** to **2** by coordinating the Pd atom on the opposite side of the C–C double bond, this occurring concomittantly to a formal 180° rotation of the ferrocene unit around the C9–C10 bond in **2**.

This isomerization of **2** to **3** involves the cleavage of at least two coordination bonds to the palladium atom. The pyridine could stabilize the almost naked palladium atom during the process, thus explaining why this isomerization was not observed under different conditions (see later). Moreover, as a result of the conformational change, the ethyl groups have different orientations with respect to the ferrocene group. Hence, it can be concluded that **2** must be the kinetic isomer of the reaction of 3-hexyne and **1** whereas **3** is the thermodynamically stable isomer. The driving force for the change of configuration of the palladocyclic unit in **2** could be based on steric grounds. The FeCp fragment may be sterically hindered by the ethyl adjacent to it, whereas in **3** this is no longer the case.

Heating the mixture of compounds **2** and **3** in pyridine at reflux temperature for 2–3 h resulted in extensive precipitation of metallic palladium. Three new products were isolated from the reaction mixture: compound **4** (ca. 60%), which does not contain palladium, and the organopalladium compounds **5** (10%) and **6** (low yield). According to its mass and NMR spectra, compound **4** was found to be the palladium-free ligand obtained from **2** or **3** via hydrolysis of the Pd–C σ bond. The new hydrogen atom on the terminal carbon atom of the butadienyl chain (triplet at 5.11 ppm) may well be derived from traces of water present in the pyridine used for the thermolysis reaction.



2 or **3** **4** (2)

Table II. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

interatomic distances		bond angles	
Pd–C10	2.259 (3)	Cl–Pd–N	89.24 (6)
Pd–C11	2.212 (3)	Cl–Pd–C13	95.18 (9)
Pd–C13	1.985 (3)	Cl–Pd–C10	154.46 (8)
Pd–N	2.239 (2)	Cl–Pd–C11	159.89 (8)
Pd–Cl	2.329 (1)	N–Pd–C10	96.05 (9)
C9–C10	1.499 (4)	N–Pd–C11	108.11 (9)
C10–C11	1.403 (4)	N–Pd–C13	167.3 (1)
C11–C12	1.503 (4)	C10–Pd–C13	85.1 (1)
C12–C13	1.326 (4)	C11–Pd–C13	65.7 (1)
C10–C16	1.534 (4)	C9–C10–C16	111.1 (2)
C11–C18	1.499 (4)	C9–C10–C11	125.3 (3)
C12–C20	1.505 (4)	C11–C12–C13	107.7 (3)
C13–C14	1.498 (4)	C5–C9–C10	128.5 (3)

Table III. Positional Parameters and Their Esd's for 5

atom	x	y	z	B,[a] Å^2
Pd	0.2085 (1)	0.20983 (7)	0.29881 (4)	3.37 (2)
Fe	0.2371 (2)	−0.1365 (2)	0.39684 (8)	5.10 (4)
Cl	0.2652 (4)	0.3450 (3)	0.2330 (1)	5.89 (9)
N	0.343 (1)	0.0847 (8)	0.2586 (4)	4.0 (2)
C1	0.051 (2)	−0.202 (1)	0.4387 (8)	9.7 (5)
C2	0.190 (2)	−0.263 (1)	0.4455 (7)	9.8 (5)
C3	0.243 (2)	−0.301 (1)	0.3950 (9)	10.0 (6)
C4	0.127 (3)	−0.257 (1)	0.3482 (8)	13.2 (5)
C5	0.015 (2)	−0.204 (1)	0.3840 (7)	10.5 (4)
C6	0.458 (1)	−0.085 (1)	0.3763 (5)	4.2 (3)
C7	0.434 (1)	−0.065 (1)	0.4323 (5)	4.7 (3)
C8	0.303 (1)	0.003 (1)	0.4359 (5)	5.0 (3)
C9	0.240 (1)	0.0301 (9)	0.3821 (4)	3.5 (2)
C10	0.339 (1)	−0.0282 (9)	0.3448 (5)	3.8 (3)
C11	0.314 (1)	−0.025 (1)	0.2842 (5)	4.7 (3)
C12	0.298 (2)	0.078 (1)	0.2009 (6)	6.6 (4)
C13	0.515 (2)	0.114 (1)	0.2655 (6)	6.5 (4)
C14	0.122 (1)	0.1146 (9)	0.3631 (4)	3.5 (2)
C15	−0.049 (1)	0.073 (1)	0.3472 (6)	5.6 (3)
C16	−0.141 (1)	0.061 (1)	0.3965 (7)	8.0 (5)
C17	0.146 (1)	0.225 (1)	0.3805 (4)	3.9 (3)
C18	0.063 (1)	0.307 (1)	0.3494 (5)	4.5 (3)
C19	0.091 (2)	0.425 (1)	0.3577 (6)	7.2 (4)
C20	0.274 (1)	0.2562 (9)	0.4230 (5)	4.0 (3)
C21	0.448 (1)	0.240 (1)	0.4140 (5)	4.2 (3)
C22	0.520 (2)	0.333 (1)	0.3823 (7)	6.5 (4)
C23	0.219 (2)	0.302 (1)	0.4690 (5)	6.7 (4)
C24	0.315 (2)	0.345 (2)	0.5187 (6)	8.7 (5)
C25	0.246 (3)	0.438 (2)	0.5410 (8)	13.6 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

interatomic distances		bond angles	
Pd–C14	2.11 (1)	Cl–Pd–N	93.9 (3)
Pd–C17	2.09 (1)	Cl–Pd–C14	167.5 (3)
Pd–C18	2.13 (1)	Cl–Pd–C17	130.3 (4)
Pd–N	2.16 (1)	Cl–Pd–C18	97.8 (3)
Pd–Cl	2.369 (3)	N–Pd–C14	98.3 (4)
C14–C17	1.44 (2)	N–Pd–C17	130.7 (5)
C17–C18	1.42 (2)	N–Pd–C18	168.2 (4)
C17–C20	1.50 (2)	C14–Pd–C18	69.9 (5)
C20–C23	1.35 (2)	C14–C17–C18	117 (1)
		C17–C20–C23	115 (1)
		Pd–C17–C20	118.6 (7)
		Pd–C14–C15	109.8 (8)
		Pd–C18–C19	122 (1)

The ^{1}H NMR spectrum of **5** is somewhat complicated since at least three signals can be detected for most of the protons (e.g. for the C_5H_5 ring and for the diastereotopic NMe_2 grouping), suggesting that **5** exists in solution as a mixture of several conformers (see Scheme I). Besides this information, the existence of a triplet at 5.28 ppm for a vinylic proton indicates that a major change as occurred on a CH_2 group. The molecular structure of **5** was determined by an X-ray diffraction study; the ORTEP diagram is shown in Figure 2. It is clear that the σ bond between the butadienyl chain Pd in **2** or **3** has been cleaved in **5** and that the former CH_2 group of the ethyl γ in **3** or **2** has

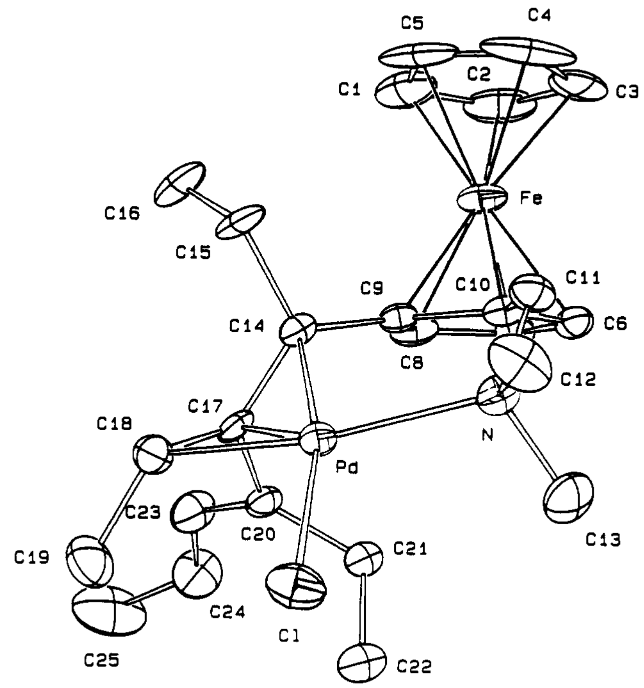


Figure 2. ORTEP view of compound **5**.

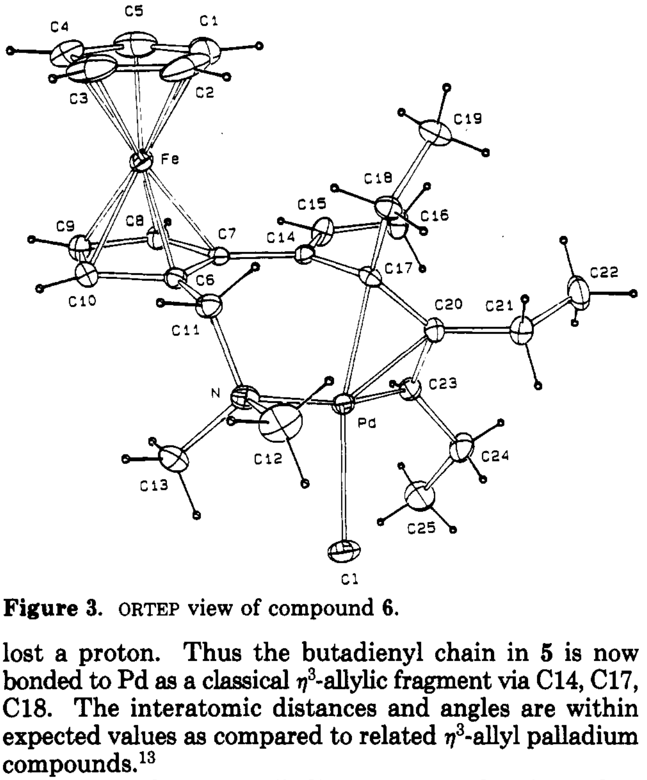


Figure 3. ORTEP view of compound **6**.

lost a proton. Thus the butadienyl chain in **5** is now bonded to Pd as a classical η^3-allylic fragment via C14, C17, C18. The interatomic distances and angles are within expected values as compared to related η^3-allyl palladium compounds.[13]

Table V. Positional Parameters and Their Esd's for 6

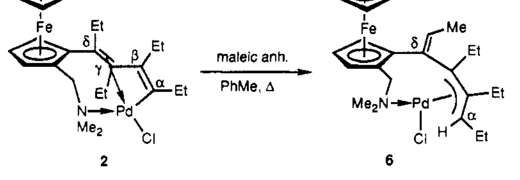
atom	*x*	*y*	*z*	*B*,[a] Å^2
Pd	0.84394 (3)	1.14745 (2)	1.23438 (4)	2.597 (6)
Fe	1.09907 (6)	0.94813 (4)	1.35187 (8)	2.79 (1)
Cl	0.7411 (1)	1.18978 (8)	1.0511 (2)	4.32 (3)
N	0.9772 (4)	1.1306 (2)	1.1061 (4)	3.18 (9)
C1	1.1570 (6)	0.9651 (5)	1.5375 (8)	7.2 (2)
C2	1.2139 (6)	1.0023 (4)	1.444 (1)	8.1 (2)
C3	1.2553 (5)	0.9502 (6)	1.3581 (8)	7.1 (2)
C4	1.2228 (6)	0.8847 (4)	1.4005 (8)	5.7 (2)
C5	1.1625 (6)	0.8936 (5)	1.5092 (7)	6.4 (2)
C6	1.0204 (4)	1.0157 (3)	1.2256 95)	2.58 (9)
C7	0.9537 (4)	0.9944 (3)	1.3357 (5)	2.17 (9)
C8	0.9493 (4)	0.9167 (3)	1.3320 (6)	3.1 (1)
C9	1.0082 (5)	0.8903 (3)	1.2224 (6)	3.5 (1)
C10	1.0508 (5)	0.9510 (3)	1.1554 (5)	3.5 (1)
C11	1.0571 (4)	1.0888 (3)	1.1781 (6)	3.0 (1)
C12	1.0218 (6)	1.2017 (4)	1.0668 (8)	5.5 (2)
C13	0.9474 (6)	1.0919 (4)	0.9813 (6)	4.8 (2)
C14	0.8939 (4)	1.0379 (3)	1.4357 (5)	2.36 (9)
C15	0.8369 (5)	1.0049 (3)	1.5305 (6)	3.5 (1)
C16	0.7764 (6)	1.0370 (4)	1.6438 (7)	4.5 (1)
C17	0.9024 (4)	1.1193 (3)	1.4310 (5)	2.57 (9)
C18	1.0049 (4)	1.1471 (3)	1.4842 (5)	3.0 (1)
C19	1.0124 (5)	1.1425 (4)	1.6391 (6)	4.2 (1)
C20	0.8103 (4)	1.1643 (3)	1.4411 (5)	3.0 (1)
C21	0.8129 (5)	1.2421 (3)	1.4944 (7)	4.1 (1)
C22	0.7639 (6)	1.2477 (4)	1.6344 (7)	5.4 (2)
C23	0.7225 (4)	1.1377 (3)	1.3768 (6)	3.2 (1)
C24	0.6216 (5)	1.1772 (4)	1.3679 (8)	4.7 (1)
C25	0.5392 (5)	1.1339 (5)	1.2939 (8)	6.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

interatomic distances		bond angles	
Pd-C17	2.155 (5)	Cl-Pd-N	92.5 (1)
Pd-C20	2.118 (6)	Cl-Pd-C17	164.7 (2)
Pd-C23	2.122 (6)	Cl-Pd-C20	125.1 (2)
Pd-N	2.166 (5)	Cl-Pd-C23	97.0 (2)
Pd-Cl	2.384 (2)	N-Pd-C17	102.6 (2)
C14-C15	1.340 (8)	N-Pd-C20	138.9 (2)
C17-C20	1.456 (8)	N-Pd-C23	165.8 (2)
C20-C23	1.393 (8)	C17-Pd-C23	68.7 (2)
C17-C18	1.517 (8)	C7-C14-C17	118.5 (5)
C20-C21	1.531 (8)	C14-C17-C20	120.4 (5)
C23-C24	1.499 (8)	C17-C20-C23	115.9 (5)
C15-C16	1.493 (9)	Pd-C17-C18	122.7 (4)
		Pd-C20-C21	117.9 (4)
		Pd-C23-C24	124.4 (5)

The second organopalladium compound **6**, formed in trace amounts in this reaction, is obtained in 55% yield by treating **2** with a large excess of maleic anhydride in refluxing toluene. The ^{1}H NMR spectra suggests that **6** is an isomer of **5**: again a vinylic and an allylic proton are found at 5.84 and 3.56 ppm, respectively. However, in contrast to **5**, which is a mixture of several conformers, **6** is a single isomeric species. It is noteworthy that prolonged heating in refluxing toluene results in the irreversible isomerization of **6** into **7**. The latter shows a ^{1}H NMR spectrum which, whilst being related to that of **6**, exhibits several important differences as far as the signals of the allylic proton, the substituted Cp ring, and the NMe$_2$ unit are concerned.



(3)

The geometry of **6** has been elucidated by crystal structure analysis (Figure 3). Here too the former butadienyl chain is interacting with the Pd center via a η^3-allylic unit, C17–C20–C23. As for **5**, a hydrogen atom is found at C23 but this time it is the CH$_2$ of the ethyl adjacent to the disubstituted Cp ring that has lost its proton; thus C15 has become an olefin carbon atom. Contrary to that in **5**, the ethyl group at C17 is in a syn position with respect to C20. The isomerization of **6** to give **7** may be rationalized

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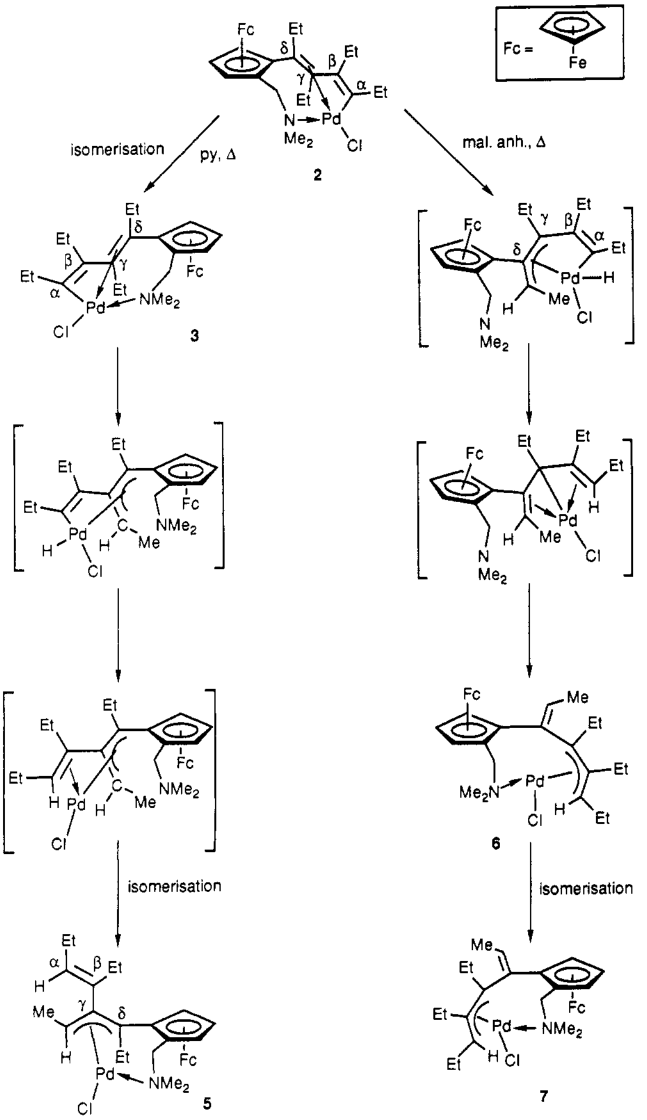
(13) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *Organometallics* **1987**, *6*, 2043. Ciajolo, R.; Jama, M. A.; Tuzi, A.; Vitagliano, A. *J. Organomet. Chem.* **1985**, *295*, 233. Ohta, T.; Hosokawa, T.; Murahashi, S. I.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080. Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013.

Scheme I. Proposed Reaction Pathways for the Formation of Compounds 5–7



by analogy with the isomerization of 2; i.e. the new isomeric form 7 can be deduced from that of 6 by an inversion of configuration of the allylpalladium unit by a rotation around C17–C14.

The formation of compounds 5 and 6 should take place according to the well-established isomerization of alkyl-substituted olefin units which are η^2-bound to a metal center.[14] It is however usually thought that this type of rearrangement should lead to a so-called 1,3-hydrogen shift. We have indeed previously[5] assigned a structure to compound 6 which derived from that of a related compound[15] obtained via such a 1,3-hydrogen shift. In the light of the crystal structure determination of 6, this is now obviously erroneous.

The result that we report here may be rationalized as being overall 1,4- and 1,5-hydrogen shifts for compounds 5 and 6, respectively. We have no evidence as to whether the hydrogen transfers occur intra- or intermolecularly. Possible reaction pathways however for the formation of 5–7 are represented in Scheme I. The first steps could therefore be akin to allylic insertion whereby allylic C–H bonds are activated by Pd(II) compounds. This process should take place on organopalladium complexes where the incoming ligands (pyridine or maleic anhydride) have perturbated the chelating effect of the terdentate ligand so as to permit the γ or δ ethyl groups to come in close proximity to the palladium center.

It was tempting to suggest that the relative conformations of 2 and 3, where the FeCp units and the CH_2 of the ethyl group in the δ and γ positions, respectively, are eclipsed, could explain the orientation of the two different reactions: i.e., the presence of the iron atom could preferentially activate the CH_2 group close to it. We have however checked that a reaction with pure compound 3 as a starting material in the presence of maleic anhydride did not afford any detectable amount of 5 after 0.5 h in refluxing toluene. We obtained instead most of the unmodified starting compound 3, together with a mixture of 6 and 7 in poor yields (<10%). Thus, the orientation of the reaction could be controlled by the incoming ligand, i.e. pyridine vs maleic anhydride, rather than by the geometry of the starting organometallic compound.

In the case of the displacement of H from 2 in the presence of maleic anhydride to give 6, the kinetic product should lead to an allylic unit for which the FeCp group is located at the central carbon atom. This situation precludes the coordination of the N atom to Pd whereas this is obviously easily achievable in 6.

The situation is slightly different for compound 3. Here the FeCp fragment on the first intermediate should be in an anti position on the allylic unit. Thus an anti–syn isomerization should then occur, being favored by the presence of large amounts of pyridine, which is the solvent of the reaction.[16]

Conclusion

Previous studies of the chemistry of polysubstituted butadienyl groups η^3-bound to a Pd center have resulted in the synthesis of new organic products with loss of the coordinated metal. These reactions arose from an activation of the substituents at the γ or δ positions of the butadienyl chain, followed by nucleophilic addition of the palladated vinyl groups to these activated substituents. In the present case, whilst an activation of the ethyl groups at the same position of the chain is still observed, the final products are however novel organopalladium compounds. One hydrogen atom is shifted from these ethyl units to the palladated vinyl groups of the starting material, thus preventing the addition of the latter groups to the activated substituents.

Experimental Section

General Considerations. All reactions were performed by using standard Schlenk tube and vacuum line techniques. All solvents used were dried[17] and distilled under N_2 prior to use. Chromatographic separations of the products were achieved on Al_2O_3 90, Activity II–III, 70–230 mesh, or on Silica gel (Kieselgel 60, 70–230 mesh) (Merck). ^1H and proton-decoupled ^{13}C NMR spectra ($CDCl_3$, 293 K, δ in ppm, J in Hz) were recorded at 200.1 and 50.3 MHz, respectively, on a Bruker SY 200 instrument, using $SiMe_4$ as reference. The $^1H^1H$ correlated 2D NMR spectrum (400 MHz, 293 K, $CDCl_3$) of compound 4 was obtained at 400 MHz with a Bruker AM 400 spectrometer. Compound 1 was prepared according to a published method,[18] 3-hexyne (Merck) was used as received.

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[14] Heck, R. F. *Organotransition Metal Chemistry*; Academic Press: New York, 1974; p 80.

[15] A 1,3-H shift was indeed observed in a related compound[10] derived from the cyclopalladated 8-methylquinolyl ligand.

[16] Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642.

[17] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratoty Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

[18] Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511.

Table VII. Crystal Parameters and Experimental Details for Compounds 3, 5, and 6

	3	5	6
formula	$C_{25}H_{36}NClFePd$	$C_{25}H_{36}NClFePd$	$C_{25}H_{36}NClFePd$
fw	548.26	548.26	548.26
cryst syst	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
space group	monoclinic	monoclinic	orthorhombic
a, Å	8.727 (1)	8.353 (2)	12.947 (3)
b, Å	27.877 (10)	12.275 (3)	18.450 (4)
c, Å	10.254 (2)	24.335 (4)	9.918 (3)
β, deg	97.44 (2)	92.58 (2)	90.00 (0)
V, Å^3	2473.9	2492.9	2369.1
Z	4	4	4
d_{calcd}, g·cm^{-3}	1.472	1.458	1.537
cryst dimens, mm	0.26 × 0.32 × 0.36	0.18 × 0.26 × 0.30	0.25 × 0.29 × 0.32
μ, cm^{-1}	14.240	14.130	14.870
scan method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg^{-1}	variable	variable	variable
scan width, deg	$0.90 + 0.34 \tan \theta$	$1.00 + 0.343 \tan \theta$	$1.00 + 0.343 \tan \theta$
θ limits, deg	2/27.5	2/24	2/27.5
octants	$\pm h,+k,+l$	$\pm h,+k,+l$	$+h,+k,+l$
no. data collcd	6101	4200	3076
no. of data with $I > 3\sigma(I)$	3810	1762	2207
abs min/max	0.84/1.33	0.74/1.31	0.84/1.06
$R(F)$	0.025	0.046	0.028
$R_w(F)$	0.035	0.061	0.038
p	0.05	0.08	0.06
GOF	1.07	1.16	0.99

Synthesis. Compound 2. A solution of 1 (768 mg; 1 mmol) and 3-hexyne (0.5 mL; 4 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature for 5 h. The solution was then reduced to 10 mL and chromatographed on silica gel (15 × 2.5 cm column; CH_2Cl_2). Compound 2 was eluted with a CH_2Cl_2–acetone mixture (95:5) (900 mg; 82%). The ^1H and ^{13}C NMR spectra were as previously reported.[3,5]

Compound 3. A solution of 2 (100 mg; 0.18 mmol) in pyridine (2 mL) was heated in an oil bath at 100 °C for 1 h, during which time the color of the solution turned from orange to orange-red. After removal of the solvent under vacuum, the residue was dissolved in Et_2O (5–10 mL) and chromatographed on alumina (10 × 2 cm column; Et_2O). Elution with Et_2O affords an orange solution which was reduced in vacuo to 5 mL. Addition of hexane (15 mL) followed by concentration in vacuo gave orange crystals of **3** (40 mg; 40%). Elution with acetone afforded unchanged **2** (53 mg).

Anal. Calcd for $C_{25}H_{36}NClFePd$: C, 54.77; H, 6.62; N, 2.55. Found: C, 54.63; H, 6.69; N, 2.49. ^1H NMR: δ 4.42, 4.30, 4.15 (3 m, 3 H, C_5H_3), 4.19 (s, 5 H, C_5H_5), 3.82 (m, 1 H, HCHMe, $^2J_{HH}$ = 16.6), 3.59, 2.53 (2 d, 2 H, CH_2N, $^2J_{HH}$ = 12.6), 2.65, 1.80 (2 s, 8 H, NMe_2 + 2HCHMe), 2.34–1.85 (m, 5 H, CH_2Me), 1.67, 1.45, 1.06, 0.93 (4 t, 12 H, CH_2CH_3, $^3J_{HH}$ = 7.5, 7.2, 7.3, 7.6). ^{13}C NMR: δ 145.2, 135.5, 117.2, 93.0 (C═C), 84.8, 54.4, 71.0, 68.9, 66.5 (C_5H_3), 69.5 (C_5H_5), 61.2 (CH_2N), 50.7, 44.5 (NMe_2), 35.0, 25.7, 24.5, 21.0 (CH_2CH_3), 16.7, 14.8, 14.0, 12.0 (CH_2CH_3).

Compounds 4 and 5. A solution of 2 (548 mg; 1.0 mmol) in pyridine (5 mL) was initially heated in an oil bath at 100 °C for 1 h and then at reflux temperature for 1.5 h (the latter leading to the formation of a Pd mirror). After removal of the solvent in vacuo, the residue was extracted with Et_2O (10 mL) and chromatographed on alumina (15 × 2.5 cm column; Et_2O). Compound **4** was obtained from the first fraction as an orange oil (245 mg; 60%). Compound **3** (28 mg) was obtained from a second band. Elution with acetone affords a yellow solution which contained **5** (50 mg; 11%) and traces (<1%) of **6**.

4. Accurate and consistent elemental analyses could not be obtained for **4**. Mass spectra: m/z 407 (M^+), 362 (11.9% of total ion), 333, 279. ^1H NMR: δ 5.11 (t, 1 H, HCEt, $^3J_{HH}$ = 7.3), 4.36, 3.86 (2 m, 2 H, C_5H_3), 4.09 (m, 6 H, C_5H_5 + C_5H_3), 3.37, 2.95 (2 d, 2 H, CH_2N, $^2J_{HH}$ = 13.2), 2.63, 2.34, 2.15, 1.98, 1.58 (5 m, 8 H, CH_2CH_3), 2.15 (s, 6 H, NMe_2), 1.21, 1.02, 0.99, 0.66 (4 t, 12 H, CH_2CH_3, $^3J_{HH}$ = 7.3, 7.4, 7.6, 7.4). ^{13}C NMR: δ 146.0, 139.3 (C═C), 129.4 (═CH), 93.5, 82.0, 70.0, 68.0, 65.4 (C_5H_3), 69.2 (C_5H_5), 57.8 (CH_2N), 45.3 (NMe_2), 31.0, 25.0, 22.6, 21.0 (CH_2CH_3), 15.6, 14.7, 13.1, 12.9 (CH_2CH_3).

5. Anal. Calcd for $C_{25}H_{36}NClFePd$: C, 54.77; H, 6.62. Found: C, 55.31; H, 6.60. ^1H NMR: δ 5.28 (t, 1 H, CHEt, $^3J_{HH}$ = 7.30), 4.23, 4.00 (2 m, 2 H, C_5H_3), 4.16–4.05 (m + 3 s of relative intensities 1/2/4, 7 H, C_5H_5 + CHMe + C_5H_3), 3.88, 3.87, 3.83, 2.77, 2.79, 2.74 (3 AB patterns, relative intensity 1/2/4, 2 H, CH_2N, $^2J_{HH}$ = 12.9, 12.9, 12.4), 2.93, 2.92, 2.89, 2.17, 2.16, 2.13 (6 s, 6 H, NMe_2), 2.47–1.88 (m, 6 H, CH_2CH_3), 1.32–1.24 (m, 3 H, $CHCH_3$), 1.07, 1.03, 0.69 (3 t, 9 H, CH_2CH_3, $^3J_{HH}$ = 7.8, 7.7, 7.5).

Compound 6. A suspension of **2** (0.82 g; 1.5 mmol) and maleic anhydride (1.5 g; 15 mmol) in toluene (30 mL) was heated at reflux temperature for 0.5 h. After removal of the solvent under vacuum, the residue was dissolved in CH_2Cl_2 (15 mL) and the solution was filtered through a Celite column (5 × 2.5 cm) to eliminate metallic palladium. The solution was reduced to 5 mL and chromatographed on alumina (15 × 2.5 cm column; Et_2O). Elution with a Et_2O–acetone (95:5) solution afforded unchanged **2**. Elution with pure acetone gave an orange solution of **6** (0.45 g; 55%). Elution with acetone–MeOH (80–20) gave **7** (60 mg; 5%). **6** was recrystallized from a CH_2Cl_2 solution layered with n-hexane.

6. Anal. Calcd for $C_{25}H_{36}NClFePd + CH_2Cl_2$: C, 49.32; H, 6.05; N, 2.12. Found: C, 49.74; H, 6.07; N, 2.22. ^1H NMR: δ 5.84 (q, 1 H, CHMe, $^3J_{HH}$ = 7.1), 4.60, 4.22, 4.11 (3 m, 3 H, C_5H_3), 4.06 (s, 5 H, C_5H_5), 4.41, 3.15 (2 d, 2 H, CH_2N, $^2J_{HH}$ = 12.6), 3.56 (dd, 1 H, CHEt, $^3J_{HH}$ = 5.6, 5.9), 2.60, 2.52 (2 s, 6 H, NMe_2), 2.75–1.70 (4 m, 6 H, CH_2CH_3), 1.49 (d, 3 H, $CHCH_3$), 1.39, 1.31, 1.09 (3 t, 9 H, CH_2CH_3, $^3J_{HH}$ = 7.5, 7.3, 7.5).

7. ^1H NMR: δ 6.05 (q, 1 H, CHMe, $^3J_{HH}$ = 7.2), 4.77, 3.15 (2 d, 2 H, CH_2N, $^2J_{HH}$ = 13.0), 4.22–4.06 (m, 4 H, C_5H_3 + CHEt), 4.17 (s, 5 H, C_5H_5), 2.85, 2.19 (2 s, 6 H, NMe_2), 2.30, 1.70 (2 m, 6 H, CH_2CH_3), 1.52 (d, 3 H, $CHCH_3$), 1.31, 1.22, 0.88 (3 t, 9 H, CH_2CH_3, $^3J_{HH}$ = 7.5, 7.4, 7.2).

Crystal Structure Determination of Compounds 3, 5, and 6. Suitable single crystals of **3**, **5**, and **6** were obtained by slow evaporation of CH_2Cl_2/n-hexane solutions at room temperature. All experimental parameters used are given in Table VII. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius MOLEN package[19] was used. All the crystallographic data were obtained on an Enraf-Nonius CAD4-F automatic diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha)$ = 0.709 30 Å) at an ambient temperature of 20 ● 2 °C. Three standard reflections were measured every 1 h during the entire data collection period for each compound. No significant changes in intensity were observed.

The raw data were converted to intensities and corrected for Lorentz and polarization factors. Semiempirical absorption

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[19] Frenz, B. A. The Enraf-Nonius CAD4-SDP. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

corrections were applied from ϕ scans of four reflections.

The structures were solved using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced in calculations in calculated positions (C–H = 0.95 Å) with isotopic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2 but were not refined. Full least-squares refinements were done; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. The absolute structure of compound **6** was determined by comparing x,y,z and $-x,-y,-z$ refinements. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from ref 20.

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Registry No. **1**, 58616-62-9; **2**, 137429-17-5; **3**, 137429-18-6; **4**, 137259-11-1; **5**, 137259-12-2; **6**, 137300-26-6; **7**, 137429-19-7; 3-hexyne, 928-49-4; maleic anhydride, 108-31-6.

Supplementary Material Available: Tables of positional parameters of the hydrogen atoms (Tables SI, SVI, SXI), bond distances (Tables SII, SVII, SXII), bond angles (Tables SIII, SVIII, SXIII), and thermal parameters (Tables SIV, SIX, SXIV) for compounds **3**, **5**, and **6**, respectively (24 pages); listings of observed and calculated structure factors for **3**, **5**, and **6** (32 pages). Ordering information is given on any current masthead page.

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(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Reactions of $(OC)_{4,3}Mn^-$ and $(OC)_{3,2}Fe^{\bullet-}$ with Alkenes, Dienes, Acetylene, and Benzene: Ground Electronic States of the Negative Ions

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$(OC)_4Mn^-$ and $(OC)_3Fe^{\bullet-}$ react with propene, 1,3-butadiene, cyclopentadiene, and benzene exclusively by η^2 addition, while allene and acetylene effect substitution competitive with addition. The high-spin triplet ground electronic state of $(OC)_4Mn^-$ is assigned on the basis of the slow rates for these reactions and its isoelectronic relationship with $Fe(CO)_4$, a triplet ground-state species. The reactions of the doubly unsaturated ions $(OC)_3Mn^-$ and $(OC)_2Fe^{\bullet-}$ ($(OC)_xM^-$) with propene and benzene form saturated adduct product ions assigned as $(OC)_xM(H)(\eta^3\text{-}C_3H_5)^-$ and $(OC)_xM(\eta^4\text{-}C_6H_6)^-$, respectively. The $(OC)_xM^-$ ions react with 1,3-butadiene to give adduct and (adduct − CO) products via excited η^4-diene intermediates. The latter branching fractions depend on the collisional quenching efficiency of the excited intermediates and the unimolecular rate of CO loss. With cyclopentadiene, the $(OC)_xM^-$ ions yield the corresponding (adduct − CO) products characterized as the $(OC)_{x-1}M(H)(\eta^5\text{-c-}C_5H_5)^-$ ions. The reactions of the $(OC)_xM^-$ ions with acetylene occur exclusively by ligand substitution terminating in the formation of the $M(C_2H_2)_x^-$ products, where M = Mn, $x = 3$, and M = Fe, $x = 2$. These product ions and the intermediate $(OC)Mn(C_2H_2)_2^-$ are shown to be the acetylene complexes rather than the corresponding metallacycles.

Inter- and intramolecular C–H bond activation studies continue to be an area of considerable interest in the chemistry of coordinatively and electronically unsaturated organometallic intermediates.[1] In the condensed phase, it has been particularly intriguing that oxidative insertion of various metal centers occurs with cyclopropyl, olefinic, and aromatic C–H bonds that have large dissociation energies.[2,3] In these reactions, the sum of the M–H and M–R bonds formed must exceed the energy of the R–H bond broken and the unfavorable entropy of the insertion process. Considerably stronger M–phenyl vs M–alkyl bonds have been observed in the $Cp^*(Me_3P)M(H)(R)$ complexes where M = Ir[4,5] or Rh[6] and Cp* = η^5-C_5Me_5; in the iridium complex, $D°(Ir–H) = 74.2$ kcal mol^{-1} and $D°$(Ir–phenyl) = 80.6 kcal mol^{-1}.[5]

It has been assumed that the ready oxidative insertion reactions into C–H bonds of alkenes and aromatics occur by prior coordination of the metal center with the π electrons followed by the oxidative insertion step.[1j,o,p,r,6,7]

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