Insertion Reactions of 1,2-Disubstituted Olefins with an α-Diimine Palladium(II) Complex

by **Carla Carfagna***[a]), **Giuseppe Gatti**[a]), **Luca Mosca**[a]), **Paola Paoli**[b]), and **Annalisa Guerri**[b])

[a]) Istituto di Scienze Chimiche, Università degli Studi di Urbino, Piazza Rinascimento 6, I-61029 Urbino (phone: +39-0722-303312; fax: +39-0722-303311; e-mail: schim@uniurb.it)

[b]) Dipartimento di Energetica, Università degli Studi di Firenze, Via S. Marta 3, I-50139 Firenze

Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

The migratory insertions of *cis* or *trans* olefins CH(X)=CH(Me) (X = Ph, Br, or Et) into the metal–acyl bond of the complex $[Pd(Me)(CO)(^iPr_2dab)]^+$ $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$ (**1**) ($^iPr_2dab$ = 1,4-diisopropyl-1,4-diazabuta-1,3-diene = *N*,*N*′-(ethane-1,2-diylidene)bis[1-methylethanamine]) are described (*Scheme 1*). The resulting five-membered palladacycles were characterized by NMR spectroscopy and X-ray analysis. Experimental data reveal some important aspects concerning the regio- and stereochemistry of the insertion process. In particular, the presence of a Ph or Br substituent at the alkene leads to the formation of highly regiospecific products. Moreover, in all cases, the geometry of the substituents in the formed palladacycle was the same as in the starting olefin, as a consequence of a *cis* addition of the Pd–acyl fragment to the C=C bond. Reaction with CO and MeOH of the five-membered complex derived from *trans*-β-methylstyrene (= [(1*E*)-prop-1-enyl]benzene) insertion, yielded the 2,3-substituted γ-keto ester **9** with an (2*RS*,3*SR*)-configuration (*Scheme 3*).

Introduction. – Insertions of unsaturated molecules into metal–C bonds represent the fundamental steps in many catalytic reactions [1]. In particular, olefin insertion into a Pd–acyl bond is a crucial step involved in several important palladium-catalyzed carbonylation processes for the synthesis of esters, ketones, and CO/alkene alternating copolymers [2][3]. Isolation of the intermediates was achieved by reaction of alkenes with palladium(II) complexes containing a chelating ligand and an acyl moiety, either pre-existent or derived from α-migration of an alkyl group to a coordinated carbon monoxide molecule [4]. In the case of ethylene as olefin, the kinetic and thermodynamic aspects of the reaction were analyzed [5], and the results were confirmed by DFT analysis [6]. Styrene [7][8] and propylene [9] insertions are the most investigated among terminal olefins, vinyl chloride was also recently employed [10]. Moreover, while several studies have been described dealing with cyclic olefins such as norbornene, norbornadiene, cyclopentene, and cycloheptene [11], to the best of our knowledge, only two examples with acyclic 1,2-disubstituted olefins are known. Diethyl fumarate and diethyl maleate insertion in an acylpalladium complex bearing a diphosphine ligand was reported [12], and reaction of (*Z*)- and (*E*)-but-2-ene with an asymmetrical phosphine-phosphitepalladium complex has been studied [9].

Here we illustrate unprecedented examples of insertion of acyclic internal olefins in the complex $[Pd(Me)(CO)(^iPr_2dab)]^+$ $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$ (**1**), where $^iPr_2dab$ = 1,4-diisopropyl-1,4-diazabuta-1,3-diene (= *N*,*N*′-(ethane-1,2-diylidene)bis[1-methylethan-

amine]). Recently, we found that complex **1** is an active catalyst in the syndiotactic CO/styrene copolymerization, and it resulted in being a useful starting point for studying the first steps of the copolymerization process [13]. The investigations described in the present work were undertaken to acquire new insight into the insertion mechanism, with the aim of evaluating how steric and electronic properties of the alkene can influence the olefin reactivity and the regio- and stereochemistry of the products. Furthermore, we describe a methodology for the selective synthesis of highly substituted carbonyl compounds.

Results and Discussion. – *X-Ray Structure of Complex* **1**. Complex **1** was synthesized by a procedure previously reported [13a]. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the compound. The palladium ion is tetracoordinated, in a square-planar fashion, by the N-atoms provided by the 1,4-diazabutadiene ligand and the C-atoms of the CO and Me ligands (*Fig. 1*). The Pd^{II} center is in the mean plane defined by the four donor atoms, the Me atom C(10) showing the highest deviation (0.133(9) Å). The length of the Pd(1)–N(2) bond, which is *trans* to the Me group, is significantly larger than that of Pd(1)–N(1), which faces the CO ligand, most probably because of the higher *trans* effect of alkyl groups relative to CO (*Table 1*). To the best of our knowledge, as established by a search in the *Cambridge Structural Database* (*CSD*, v. 5.27, November 2005) [14], this is the second example of a tetracoordinated Pd complex featuring both the CO and the Me group in the coordination sphere characterized by X-ray crystallography. However, the first one reported by *Setsune* and co-workers [15] is affected by a positional disorder between the CO and the Me ligands, thus preventing any reliable structural comparison concerning the Pd coordination sphere.

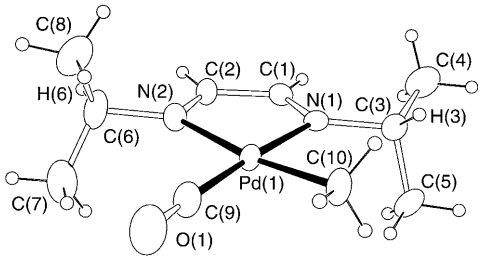


Fig. 1. *ORTEP3 view of the complex cation of* **1**. All atoms are drawn at 40% probability, except for H-atoms, which were assigned arbitrary thermal parameters.

As to the $^{i}Pr_2$dab ligand, it appears that the two isopropyl groups are not iso-oriented with respect to the α-diimine moiety: across the C(6)–N(2) bond, both Me groups of the ^{i}Pr group that faces the less bulky CO are *gauche*-positioned (*ca.* $\pm 60^{\circ}$) with respect to the Pd ion. Instead, across the C(3)–N(1) bond, the atoms C(5) and H(3) are *gauche* with respect to the central atom, possibly to minimize the steric repulsion with the facing Me group, as already hypothesized for a Pd^{II} complex with the same diaza ligand [16].

Table 1. *Selected Bond Distances* [Å] *and Angles* [°] *of the Coordination Sphere for Compounds* **1**–**4**

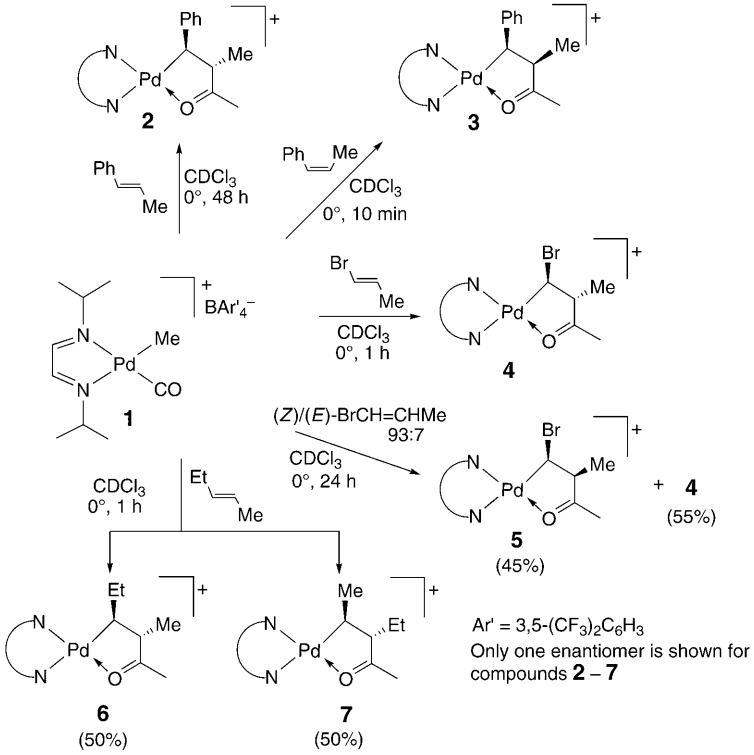
	1	**2**	**3**	**4**
Pd(1)–N(1)	2.089(6)	2.033(4)	2.037(3)	1.98(1)
Pd(1)–N(2)	2.140(5)	2.149(4)	2.129(3)	2.08(2)
Pd(1)–C(9)	1.87(1)			
Pd(1)–C(10)	2.035(7)			
Pd(1)–O(1)		2.054(3)	2.057(2)	2.05(1)
Pd(1)–C(13)		2.043(5)	2.030(4)	2.00(2)
N(1)–Pd(1)–N(2)	78.3(2)	79.1(2)	79.2(1)	80.0(6)
C(9)–Pd(1)–N(1)	176.8(3)			
C(9)–Pd(1)–N(2)	103.8(3)			
C(9)–Pd(1)–C(10)	82.6(3)			
C(10)–Pd(1)–N(1)	95.5(3)			
C(10)–Pd(1)–N(2)	172.0(3)			
N(1)–Pd(1)–O(1)		176.0(2)	177.8(1)	178.2(6)
N(1)–Pd(1)–C(13)		100.0(2)	100.2(2)	100.7(7)
O(1)–Pd(1)–N(2)		99.0(2)	98.9(1)	98.4(6)
C(13)–Pd(1)–N(2)		176.9(2)	176.9(2)	178.7(7)
C(13)–Pd(1)–O(1)		82.1(2)	81.9(1)	81.0(7)

Insertion Reactions and Structures of Palladacycles **2**–**7**. Insertion of *cis*- or *trans*-1,2-disubstituted alkenes into the Pd–acyl bond was achieved by reaction of **1** in $CDCl_3$ at 0° with a 10:1 excess of one of the following olefins: *trans*-*β*-methylstyrene (=[(1*E*)-prop-1-enyl]benzene), *cis*-*β*-methylstyrene (=[(1*Z*)-prop-1-enyl]benzene), (1*E*)-1-bromoprop-1-ene, a 93:7 mixture of (1*Z*)- and (1*E*)-1-bromoprop-1-ene isomers (as furnished by *Aldrich*), and (2*E*)-pent-2-ene (*Scheme 1*). By using (2*Z*)-pent-2-ene, a complete isomerization to the (2*E*) form was observed before the insertion reaction took place. A large excess of olefin with respect to the Pd complex **1** was required to prevent decomposition reactions. Formation of black Pd precipitate was observed when a stoichiometric amount of the alkene was employed.

The progress of the reactions was monitored by analysis of ^{1}H-NMR spectra following the disappearance of the Me–Pd signal of complex **1** and the concomitant increase of an acetyl peak at *δ ca.* 2.4. After complete consumption of complex **1**, the solvent was evaporated, and the resulting products were washed with hexane. With *trans*-*β*-methylstyrene, *cis*-*β*-methylstyrene, and (1*E*)-1-bromoprop-1-ene, exclusive formation of compounds **2**, **3**, and **4**, respectively, was observed. In the case of the 93:7 mixture of (1*Z*)- and (1*E*)-1-bromoprop-1-ene, due to the higher reactivity of the (1*E*) isomer (*vide infra*), both compounds **5** and **4** were obtained in a 45:55 ratio. With (2*E*)-pent-2-ene, a brown oil was isolated, which was an equimolar mixture of complexes **6** and **7** (*Scheme 1*).

The individuation of the spin system C*H*(X)C*H*(*Me*) (X=Ph, Br, or Et) and of an acetyl fragment in the ^{1}H- and ^{13}C-NMR spectra of all complexes **2**–**7** confirmed the olefin insertion. The coordination of the Ac O-atom to the metal was established by the presence of a very deshielded carbonyl signal (at $\delta > 238$) together with an IR stretching band at *ca.* 1600 cm^{-1} [4][17]. The regiochemistry was determined by means of 2D heteronuclear correlation experiments based on ^{1}H,^{13}C long-range cou-

Scheme 1[a])



[a]) Reaction conditions: 100 mg of complex **1**; V_{tot} (solvent + olefin) = 1 ml; olefin/Pd molar ratio 10 : 1.

plings and NOE measurements. Thus, the proximity of the CH(Me) fragment to the acetyl moiety in compounds **2**–**6** was inferred by the observation of the ^3J(CH) couplings *C*H(Me)C(O)*Me* and CH(*Me*)*C*(O)Me. In complex **7**, this type of couplings, being ^4J, were not observed. The presence of an NOE enhancement CH(*Me*)/*Me*C(O) was further evidence for the structure of compounds **2**–**6**. For determining the configuration, we exploited the considerable difference in the NOE enhancements C*H*(X)/C*H*(Me) observed in the pairs **2** and **3**, and **4** and **5**; the *cis* isomer was assigned to the higher enhancement.

The structural assignment for compounds **2**–**4** was fully confirmed by X-ray solid-state analyses (*Fig. 2*). Crystals of compounds **2** and **3** are almost isomorphous, and both their asymmetric units contain one complex cation and one counterion; the same content holds for the asymmetric unit of **4**. Concerning compounds **2** and **3**, the two metal complexes are practically superimposable, with the obvious exception of the Me atom C(12): the Ph rings are nearly perpendicular to the Pd^{II} coordination plane and face the 1,4-diazabuta-1,3-diene ligand (*Fig. 2*). In all the complexes, Pd^{II} is tetracoordinated, in a square-planar geometry, by the two N-atoms of the $^iPr_2$dab ligand, the Ac atom O(1), and the atom C(13). As already pointed out for **1**, even in these complexes, the Pd–N

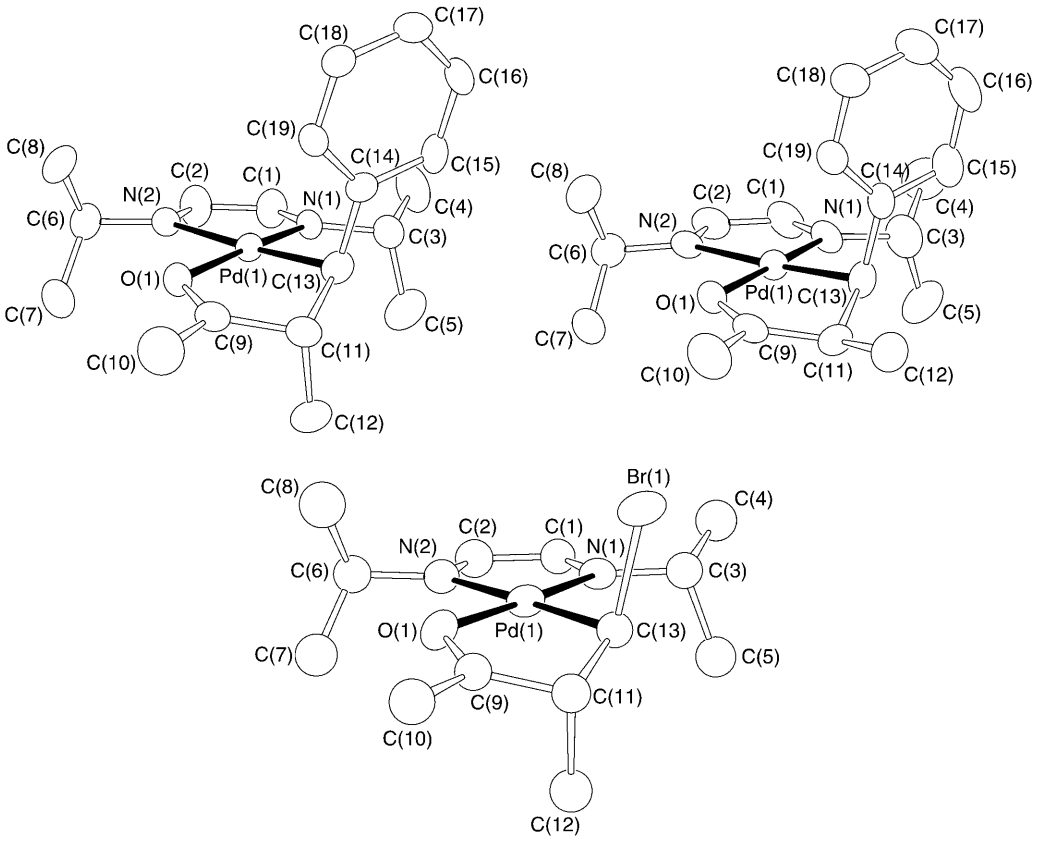


Fig. 2. *ORTEP3 view of the complex cations of* **2** (left), **3** (right), *and* **4** (below). All atoms are drawn at 40% probability; H-atoms are omitted for the sake of clarity.

bond in *trans* position to the Pd–alkyl bond is significantly longer with respect to the bond facing the Ac O-atom (*Table 1*).

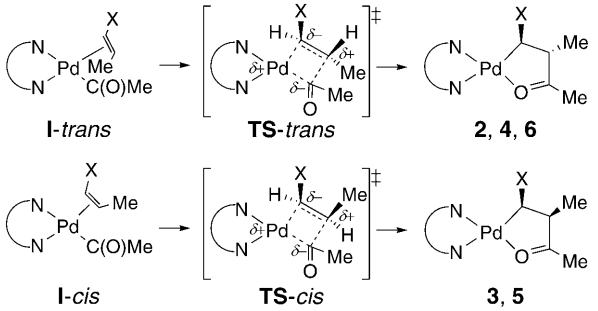
The conformation (with respect to the 1,4-diazabuta-1,3-diene skeleton) of the ^{i}Pr groups is almost identical and superimposable to that found in **1** for all the complexes. The two Me groups opposite the O-atom point toward the palladacycle, while the atoms C(5) and H(3), facing the C-atom bearing the Ph or Br substituent, are *gauche*-positioned with respect to the central atom.

On the basis of the experimental results, we were able to draw some important considerations: *i*) in all palladacycles, the relation (*cis* or *trans*) between the Ph, Br, or Et substituents and the vicinal Me group corresponds to that in the starting olefin ((*Z*) or (*E*)). *ii*) The regioselectivity of the insertion reaction depends on the nature of the olefin substituents: in complexes **2**–**5**, the Ph or Br substituent is exclusively at the C-atom in α position to the Pd-atom, while with pent-2-ene, a nearly equimolar mixture of the two regioisomers **6** and **7** is obtained. *iii*) Reaction rates are strictly related not only to the olefin employed, but also to its configuration; the following order of reactivity can

be derived from a comparison of the reaction times: *cis*-β-methylstyrene > (1*E*)-1-bromoprop-1-ene ≈ (2*E*)-pent-2-ene ≫ (1*Z*)-1-bromoprop-1-ene > *trans*-β-methylstyrene.

These findings can be rationalized on the basis of general accepted mechanisms. As previously observed in analogous reactions with ethylene [5][6] or terminal olefins [7a][9], the formation of compounds **2**–**7** should include α-migration of the Me ligand in complex **1**, olefin coordination (intermediates **I**-*trans* and **I**-*cis* in *Scheme 2*), and olefin insertion passing through a concerted *cis* addition of the Pd–acetyl fragment to the C=C bond. The resulting four-membered transition states **TS**-*trans* and **TS**-*cis* (*Scheme 2*) account for the conservation of the *trans* or *cis* geometry of the substituents in compounds **2**–**7**.

Scheme 2



The high regioselectivity observed in the insertion of β-methylstyrene and 1-bromoprop-1-ene is presumably due to the concurrence of steric and electronic factors. The hindrance between the Ph or Br substituents and the migrating Ac moiety induces the latter to bind to the Me-substituted olefin C-atom [3a][18]. A comparison of the volumes of the Ph, Br, and Me substituent, 68, 31, and 21 Å^3, respectively, evaluated by means of the search-compare module of Insight-II [19], supports this hypothesis. In addition, as estimated by the *Merz–Singh–Kollman* (*MK*) [20] charge-derivation scheme (implemented in Gaussian 03, revision B.05), the CH(X) olefin C-atom, with X = Ph or Br, is negatively charged, while the other alkene C-atom is positive, and a significant polarization of the C=C bond (*ca.* 0.7e) is present. Thus, given that the bonding of the Pd-atom to the more negative olefin C-atom (*Scheme 2*) should be favored [21], both these data justify the observed regioselectivity.

In the case of pent-2-ene, for steric reasons (34 Å^3 is the estimated volume of the Et group), the Ac group should bind preferentially to the Me-substituted olefin C-atom. However, from the computation of the atomic charges, both the olefin C-atoms have a negative charge assigned (the Et-substituted C-atom is the most negative) and the C=C bond is less polarized (*ca.* 0.4e) with respect to that of β-methylstyrene and bromo-1-propene. Thus the lack of regioselectivity in the pent-2-ene insertion could be related to a vague difference in terms of electron density between the two olefin C-atoms.

Concerning the reactivity, a remarkable difference in the reaction times between the (*Z*)- and the (*E*)-form of the same olefin appears evident. Insertion of *cis*-β-methylstyrene occurs within a few minutes, while the reaction of the *trans* isomer is com-

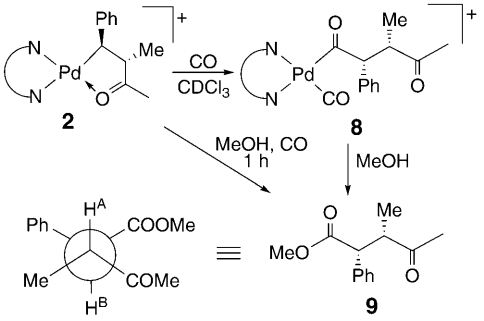
pleted only after two days. In the case of bromo-1-propene, instead, the (*E*)-isomer appears to be more reactive than the (*Z*)-isomer. Apparently, the activation energies involved in the insertion process are differently influenced by the geometry and the type of the olefin substituents [22].

Reactivity of Complex **2** *with Carbon Monoxide.* To check whether the five-membered palladacycles **2**–**7** could be intermediates for the synthesis of highly substituted carbonyl compounds, we studied their reactivity with carbon monoxide. Bubbling CO in a $CDCl_3$ solution of **2** at $-30°$ quickly led to open-chain complex **8** (*Scheme 3*). No reaction was observed with complexes **3**–**7**, even after bubbling CO through their solution for a long time. The inertness of compounds **4** and **5** can be ascribed to the presence of the electron-withdrawing Br substituent, which produces both a tight chelation (confirmed by shorter Pd(1)–C(13) and Pd(1)–O(1) bond distances of **4** with respect to those of **2** and **3**) and a low migratory aptitude of the CH(Br)CH(Me)C(O)Me fragment [10].

The structure of complex **8** is highlighted by three CO chemical shifts observed in the ^{13}C-NMR spectra: one at δ 171.9, due to the CO coordinated to Pd, and the other two at $\delta > 200$, due to the acyl-moiety CO of the open chain. This assignment is further confirmed by the presence of three IR bands, one of which (2130 cm^{-1}) is typical of a CO ligand bonded to a metal center.

Methanolysis of the Pd–acyl bond of complex **8** afforded the γ-keto ester **9** which, according to the ^{1}H- and ^{13}C-NMR spectra, was established to be just one diastereoisomer. The vicinal coupling constants between H^A and H^B is 11.2 Hz, in agreement with a locked conformation, with these two H-atoms in *anti*-periplanar position (see *Newman* projection in *Scheme 3*). Observation of an NOE enhancement between the Me group and the H_o-atom of the Ph substituent indicates that compound **9** has the (2*RS*,3*SR*) configuration, corresponding to a retention of configuration with respect to **2**.

Scheme 3



Only one enantiomer is shown for compounds **2**, **8**, and **9**

Conclusions. – We have isolated and fully characterized, for the first time, intermediates derived from the insertion of 1,2-substituted acyclic olefins in the Pd–acyl bond of an (α-diimine)palladium complex. We found that the presence of a Ph or Br substituent at the C=C bond leads to the formation of highly regiospecific products,

due to both steric and electronic factors. Moreover, all the reported examples confirm a *cis* addition of the Pd-atom and acyl group to the olefin through a four-membered concerted transition state, allowing the synthesis of palladacycles with a defined geometry concerning the substituents. Previously described reactions with diethyl maleate, diethyl fumarate [12], and but-2-ene [9] instead produce mixtures of *cis* and *trans* compounds. Starting from *trans*-β-methylstyrene, we synthesized a γ-keto ester deriving from the methoxycarbonylation of the palladacycle. The acquired knowledge can be applied to the synthesis of highly substituted carbonyl compounds with a specific geometry.

This work was supported by the *Ministero dell'Istruzione, dell'Università e della Ricerca* (*MIUR Rome*; PRIN N° 2003039774). CRIST (Centro Interdipartimentale di Cristallografia Strutturale), University of Florence, where the X-ray measurements were performed, is gratefully acknowledged. Thanks are due to Dr. *Andrea Ienco* of ICCOM-CNR (Florence) for the quantum-chemical calculations carried out by using the high performance systems at the Centro di Calcolo Interuniversitario CINECA (CNR-CINECA agreement) and to Mrs. *Anna Rita Pierleoni* for technical assistance.

Experimental Part

General. All manipulations were carried out under N_2 by using *Schlenk* techniques. CP-Grade chemicals were used as received unless otherwise stated. Solvents were dried by standard methods and freshly distilled under N_2. $CDCl_3$ was degassed and stored over 3-Å molecular sieves. $[Pd(Me)(CO)(^iPr_2dab)]^+[BAr'_4]^-$ (**1**) ($^iPr_2dab$ = 1,4-diisopropyl-1,4-diazabuta-1,3-diene; Ar′ = 3,5-$(CF_3)_2C_6H_3$) was synthesized as previously reported [13a]. *trans*- and *cis*-β-Methylstyrene, (1*E*)- and (1*Z*)-1-bromoprop-1-ene, (2*Z*)-pent-2-ene were purchased from *Aldrich*, while (2*E*)-pent-2-ene was purchased from *Lancaster*. Carbon monoxide (CP grade 99.99%) was supplied by *Air Liquide*. IR Spectra: *Nicolet-FT-IR-Avatar-360* spectrometer; in cm^{-1}; range 4000–600 cm^{-1}. NMR Spectra: *Bruker-AC200* spectrometer with a multinuclear 5-mm probehead, δ in ppm rel. to $SiMe_4$ measured by using the residual ^1H or ^{13}C resonance of the deuterated solvents, *J* in Hz. Elemental analyses (C, H, N): *Fisons-Instruments-1108-CHNS-O* elemental analyzer.

Data of the Counterion Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) ($[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$) *of* **2**–**8** ^1H-NMR ($CDCl_3$, 20°): 7.71 (*s*, 8 H_o); 7.54 (*s*, 4 H_p). ^{13}C-NMR ($CDCl_3$, 20°): 161.7 (*q*, ^1J(C,B) = 49.3, C_{ipso}); 134.8 (C_o); 128.8 (*q*, ^2J (C,F) = 31.2, C_m); 124.6 (*q*, ^1J (C,F) = 270.8, CF_3); 117.5 (C_p).

Synthesis of Complexes **2**–**7**. Compound **1** (100 mg, 86.7 μmol) was dissolved in $CDCl_3$ in an NMR tube, and (*Z*)- or (*E*)-olefin (0.87 mmol; olefin/Pd molar ratio 10:1) was added, the total soln. volume was 1 ml. The soln. was kept at 0° and monitored by NMR spectroscopy until the signals relative to the starting Pd complex **1** completely disappeared. Then, the soln. was filtered through *Celite*, and the solvent was evaporated *i.v.* The resulting solid was washed with hexane (2 × 3 ml) and dried under vacuum to yield, depending on the starting olefin, palladacycles **2**–**7**.

*(*SP*-4-2)-{*N,N′*-(Ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]}[(1*RS*,2*RS*)-2-methyl-3-(oxo-*κ*O)-1-phenylbutyl-*κ*C]palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*trans*-[Pd(CH(Ph)CH(Me)C(O)Me)($^iPr_2dab$)]$^+$[BAr'_4]$^-$; **2**). Reaction time 48 h, yield 78.2 mg (71%). Orange solid. IR (nujol): 1621 (C=O), 1610 (C=N). ^1H-NMR ($CDCl_3$, 20°): 7.81, 7.67 (2*s*, 2 CH=N); 7.33–7.22 (*m*, Ph); 3.88 (*sept.*, *J* = 6.4, 1 Me_2CH); 3.42 (*d*, *J* = 3.6, PhC*H*); 3.38 (*sept.*, *J* = 6.4, 1 Me_2CH); 2.80 (*dq*, *J* = 3.6, 7.4, MeC*H*); 2.49 (*s*, MeCO); 1.47 (*d*, *J* = 7.4, *Me*CH); 1.32, 1.28, 1.21, 0.93 (4*d*, *J* = 6.4, 2 Me_2CH). ^{13}C-NMR ($CDCl_3$, 20°): 240.9 (Me*C*O); 161.8, 156.4 (C=N); 144.4 (C_{ipso}); 129.6, 126.8 (C_o, C_m); 127.3 (C_p); 62.4 (Me*C*H); 62.4, 57.5 (Me_2CH); 53.2 (Ph*C*H); 27.2 (*Me*CO); 23.6, 21.5, 21.4, 20.7 (Me_2CH); 17.8 (*Me*CH). Anal. calc. for $C_{51}H_{41}BF_{24}N_2OPd$ (1271.06): C 48.19, H 3.25, N 2.20; found: C 47.90, H 3.06, N 2.16.

*(*SP*-4-2)-{*N,N′*-(Ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]}[(1*RS*,2*SR*)-2-methyl-3-(oxo-*κ*O)-1-phenylbutyl-*κ*C)palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*cis*-[Pd(CH(Ph)-

CH(Me)C(O)Me)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **3**). Reaction time 10 min. Yield 67.0 mg (61%). Red solid. IR (nujol): 1610 (C=O), 1610 (C=N). ^{1}H-NMR ($CDCl_3$, 20°): 7.83, 7.75 (2*s*, 2 CH=N); 7.35–7.18 (*m*, 2 H_m, H_p); 7.08–7.02 (m, 2 H_o); 4.04, 3.87 (2 *sept.*, *J* = 6.5, 2 Me_2CH); 3.64 (*d*, *J* = 7.5, PhC*H*); 3.33 (*dq*, *J* = 7.0, 7.5, MeC*H*); 2.46 (*s*, *Me*CO); 1.37, 1.36, 1.27, 1.06 (4*d*, *J* = 6.5, 2 Me_2CH); 1.07 (*d*, *J* = 7.0, *Me*CH). ^{13}C-NMR ($CDCl_3$, 20°): 239.9 (Me*C*O); 161.6, 156.3 (C=N); 140.9 (C_{ipso}); 129.8, 126.9 (C_o, C_m); 127.2 (C_p); 62.6, 58.7 (Me_2CH); 59.5 (MeCH); 54.0 (PhCH); 28.3 (*Me*CO); 23.3, 21.6, 21.5 (Me_2CH); 14.4 (*Me*CH). Anal. calc. for $C_{51}H_{41}BF_{24}N_2OPd$ (1271.06): C 48.19, H 3.25, N 2.20; found: C 47.97, H 2.99, N 2.19.

*(*SP*-4-2)-[(1*RS*,2*RS*)-1-Bromo-2-methyl-3-(oxo-*κ*O)butyl-*κ*C][*N,N′*-(ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]]palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*trans*-[Pd(CH(Br)CH(Me)C(O)Me)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **4**). Reaction time 1 h. Yield 97.5 mg (88%). Yellow solid. IR (film): 1624 (C=O), 1609 (C=N). ^{1}H-NMR (CD_2Cl_2, −30°): 7.99, 7.95 (2*s*, 2 CH=N); 4.05, 3.91 (2 *sept.*, *J* = 6.5, 2 Me_2CH); 3.89 (*s*, BrCH); 3.34 (*q*, *J* = 7.6, MeC*H*); 2.55 (*s*, *Me*CO); 1.52 (*d*, *J* = 7.6, *Me*CH); 1.43, 1.41, 1.37, 1.27 (4*d*, *J* = 6.5, 2 Me_2CH). ^{13}C-NMR (CD_2Cl_2, −30°): 241.1 (Me*C*O); 163.0, 158.5 (C=N); 65.2 (MeCH); 63.1, 60.7 (Me_2CH); 54.5 (BrCH); 27.8 (*Me*CO); 23.7, 21.4, 21.3, 20.9 (Me_2CH); 19.3 (*Me*CH). Anal. calc. for $C_{45}H_{36}BBrF_{24}N_2OPd$ (1273.86): C 42.43, H 2.85, N 2.20; found: C 41.88, H 2.71, N 2.11.

*(*SP*-4-2)-[(1*RS*,2*SR*)-1-Bromo-2-methyl-3-(oxo-*κ*O)butyl-*κ*C][*N,N′*-ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]]palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*cis*-[Pd(CH(Br)CH(Me)C(O)Me)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **5**). Reaction time 24 h. Yield 85.9 mg (78%). Yellow-green powder corresponding to a 55:45 mixture **4**/**5**. IR (film): 1622 (C=O), 1608 (C=N). Anal. calc. for $C_{45}H_{36}BBrF_{24}N_2OPd$ (1273.86): C 42.43, H 2.85, N 2.20; found: C 41.57, H 2.78, N 2.10.

The NMR signals arising from **5** were assigned by subtracting the NMR spectra of **4** from those of the mixture. ^{1}H-NMR (CD_2Cl_2, −30°): 7.99, 7.96 (2*s*, 2 CH=N); 4.23 (*d*, *J* = 4.2, BrCH); 4.07, 3.92 (2 *sept.*, *J* = 6.5, 2 Me_2CH); 3.50 (*dq*, *J* = 6.8, 4.2, MeC*H*); 2.47 (*s*, MeCO); 1.50 (*d*, *J* = 6.8, *Me*CH); 1.44, 1.39, 1.36, 1.29 (4*d*, *J* = 6.5, 2 Me_2CH). ^{13}C-NMR (CD_2Cl_2, −30°): 238.3 (Me*C*O); 162.8, 158.4 (C=N); 58.8 (MeCH); 63.0, 60.9 (Me_2CH); 61.3 (BrCH); 29.4 (*Me*CO); 23.7, 22.2, 21.4, 21.3 (Me_2CH); 16.2 (*Me*CH).

*(*SP*-4-2)-{*N,N′*-(Ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]}[(1*RS*,2*SR*)-1-ethyl-2-methyl-3-(oxo-*κ*O)butyl-*κ*C)palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*trans*-[Pd(CH(CH$_2$Me)CH(Me)C(O)Me)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **6**) *and (*SP*-4-2)-{*N,N′*-(Ethane-1,2-diylidene)-bis[1-methylethanamine-*κ*N]}[(1*RS*,2*SR*)-2-ethyl-1-methyl-3-(oxo-*κ*O)butyl-*κ*C)palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (*trans*-[Pd(CH(Me)CH(CH$_2$Me)C(O)Me)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **7**). Reaction time 1 h. Yield 99.2 mg (94%) of **6**/**7** 1:1. Yellow-brown oil. IR (film): 1620 (C=O), 1610 (C=N). Anal. calc. for $C_{47}H_{41}BF_{24}N_2OPd$ (1223.02): C 46.16, H 3.38, N 2.29; found: C 44.60, H 3.67, N 2.01.

Data of **6**: ^{1}H-NMR ($CDCl_3$, 20°): 7.86 (*s*, 2 CH=N); 3.97–3.77 (*m*, 2 Me_2CH); 2.41 (*s*, *Me*CO); 2.38–2.26 (*m*, MeC*H*, $MeCH_2CH$); 1.55 (*d*, *J* = 7.6, *Me*CH); 1.34–1.20 (*m*, 2 Me_2CH); 1.26–1.18 (*m*, MeCH_2CH); 0.96 (*t*, *J* = 7.2, *Me*CH_2CH). ^{13}C-NMR ($CDCl_3$, −20°): 242.1 (Me*C*O); 162.1, 156.1 (C=N); 62.8, 59.4 (Me_2CH); 59.6 (MeCH); 56.9 ($MeCH_2CH$); 29.7 (MeCH_2CH); 27.1 (*Me*CO); 23.9, 21.7, 21.5, 20.7 (Me_2CH); 20.0 (*Me*CH); 13.2 (*Me*CH_2CH).

Data of **7**: ^{1}H-NMR ($CDCl_3$, 20°): 7.86 (*s*, 2 CH=N); 3.97–3.77 (*m*, 2 Me_2CH); 2.55–2.35 (*m*, MeC*H*); 2.42 (*s*, *Me*CO); 2.14–1.94 (*m*, $MeCH_2CH$); 1.98–1.90 (*m*, MeCH_2CH); 1.34–1.20 (*m*, 2 Me_2CH); 1.14 (*t*, *J* = 7.2, *Me*CH_2CH); 0.78 (*d*, *J* = 7.6, *Me*CH). ^{13}C-NMR ($CDCl_3$, −20°): 241.4 (Me*C*O); 162.1, 156.1 (C=N); 69.8 ($MeCH_2CH$); 62.8, 59.4 (Me_2CH); 46.4 (MeCH); 28.1 (*Me*CO); 27.4 (MeCH_2CH); 23.9, 21.7, 21.5, 20.7 (Me_2CH); 22.3 (*Me*CH); 12.3 (*Me*CH_2CH).

*(*SP*-4-3)-Carbonyl{*N,N′*-(ethane-1,2-diylidene)bis[1-methylethanamine-*κ*N]}[(2*RS*,3*SR*)-3-methyl-1,4-dioxo-2-phenylpentyl-*κ*C]palladium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* ([Pd(C(O)CH(Ph)CH(Me)C(O)Me)(CO)(^{i}Pr$_2$dab)]$^+$[BAr′$_4$]$^-$; **8**). Bubbling CO at −30° for 3 min into a $CDCl_3$ soln. (0.6 ml) of **2** (50 mg) resulted in the formation of **8**. This complex was stable only in soln. and for a few hours. IR ($CDCl_3$): 2130 (C≡O); 1751, 1713 (C=O); 1612 (C=N). ^{1}H-NMR ($CDCl_3$, −10°): 7.79 (*s*, 2 CH=N); 7.46–7.20 (br. *m*, Ph); 4.43 (*d*, *J* = 10.5, PhC*H*); 3.70 (*sept*., *J* = 6.0, 2 Me_2CH); 3.49 (*dq*, *J* = 7.3, 10.5, MeC*H*); 2.33 (*s*, *Me*CO); 1.17, 1.04 (2*d*, *J* = 6.0, 2 Me_2CH); 0.95 (*d*,

$J = 7.3$, *Me*CH). ^{13}C-NMR ($CDCl_3$, $-55°$): 212.3, 211.9 (PhCHCO, MeCO); 171.9 (Pd–CO); 163.5, 159.5 (C=N); 131.4 (C_{ipso}); 130.8, 130.3, 130.1 (C_o, C_m, C_p); 70.1, 63.3 (Me_2CH); 59.9 (PhCH); 49.5 (MeCH); 29.3 (*Me*CO); 22.6, 22.4, 21.6 (Me_2CH); 15.3 (*Me*CH).

*(2*RS*,3*SR*)-3-Methyl-4-oxo-2-phenylpentanoic Acid Methyl Ester* (MeOC(O)CH(Ph)CH(Me)-C(O)Me; **9**) Complex **2** (78.2 mg, 61.5 μmol) was dissolved in MeOH (1.5 ml), then CO was bubbled at r.t. for 5 min. Formation of a black Pd precipitate was observed. The mixture was stirred for 1 h at 20° and then concentrated *i.v.*. The residue was purified by column chromatography (silica gel, hexane/AcOEt 6:4): **9** (12.3 mg, 91%). Yellow oil. The same product was also obtained by bubbling CO in a $CHCl_3$ soln. of **2**, with formation of **8**, and then adding MeOH.

Data of **9**: IR (film): 1732 (C=O, ester), 1715 (C=O, ketone). ^{1}H-NMR ($CDCl_3$, 20°): 7.39–7.22 (*m*, Ph); 3.81 (*d*, $J = 11.2$, PhC*H*); 3.61 (*s*, *Me*OOC); 3.30 (*dq*, $J = 7.3$, 11.2, MeC*H*); 2.29 (*s*, *Me*CO); 0.88 (*d*, $J = 7.3$, *Me*CH). ^{13}C-NMR ($CDCl_3$, 20°): 211.9 (Me*C*O); 174.1 (MeO*C*); 136.8 (C_{ipso}); 128.9, 128.6 (C_o, C_m); 127.7 (C_p); 53.6 (*Me*OOC); 52.2 (Ph*C*H); 49.4 (Me*C*H); 29.0 (*Me*CO); 14.6 (*Me*CH). Anal. calc. for $C_{13}H_{16}O_3$ (220.27): C 70.89, H 7.32; found: C 72.05, H 6.91.

X-Ray Crystallography[1]). Crystals of compounds **1**–**4** were obtained by slow diffusion of hexane into a CH_2Cl_2 soln. of the corresponding salts. Crystallographic data for **1** were collected on a *Siemens-Smart* diffractometer equipped with a rotating anode and controlled by using the SMART [23] software. The radiation used was CuK_α (λ 1.5418 Å), and intensity data were acquired at 200 K. Five settings of ω were used, and narrow data 'frames' were collected for 0.3° increments in ω. A total of 3000 frames of data were stored providing a sphere of data. Data reduction was performed with the SAINT 4.0 program [24]. Absorption correction to all data was applied (SADABS) [25]. Data collection on suitable crystals of compounds **2**–**4** were carried out on an *Oxford-Diffraction-Excalibur* diffractometer with MoK_α radiation (λ 0.7107 Å) equipped with a CCD area detector and a cryocooling device by *Oxford Cryosystem* which was used to set the temp. at 150 K for all the experiments. Data collections were performed with the CrysAlis CCD program [26]. For all the crystals, six runs of data were collected, five of which for 1° increment in ω, while the last for 1° increment in φ. Around 300 frames of data were collected providing a sphere of data. Data reduction was carried out with the CrysAlis RED program [27]. Absorption correction was applied through the ABSPACK program [28]. Crystals of compound **4** are twinned. The twin law is represented by the matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$; this is one of the most frequently encountered twin laws in which a monoclinic symmetry with the β angle of *ca.* 90° emulates orthorhombic symmetry. The BASF (fractional contributions of the various twin components) parameter was refined, and its final value is 0.337(3). All structures were solved with the SIR97 program [29], and then refined with the SHELX97 program [30]. The F-atoms of the counter anion were disordered, as often found for this species [31]. Anisotropic thermal parameters were used for all non-H-atoms for compounds **1**–**3**, while in **4** the C-atoms were also treated isotropically. All the H-atoms were introduced in calculated position and refined with a temp. factor depending on the one of the atom to which they are bound. Geometrical calculations were performed by PARST97 [32], and molecular plots were produced by the ORTEP3 program [33]. Details of the crystal data, data collection, structure solution, and refinement are reported in *Table 2*.

Computational Details. The GAUSSIAN03 (Revision B.05) [34] package implemented on a personal computer was used. In all cases, the level of theory was HF-SCF, the basis set was 6–311G(d,p) [35], and the *Berny* algorithm was used [36]. The reliability of the stationary point was assessed by the evaluation of the vibrational frequencies.

---

[1]) CCDC-297683, -297684, -297685, and -297686 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif from the *Cambridge Crystallographic Data Centre.*

Table 2. *Data Collection and Refinement Parameters for Compounds* **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{42}H_{31}BF_{24}N_2OPd$	$C_{51}H_{41}BF_{24}N_2OPd$	$C_{51}H_{41}BF_{24}N_2OPd$	$C_{45}H_{36}BBrF_{24}N_2OPd$
M_r	1152.90	1271.07	1271.07	1273.88
Temp. [K]	200	150	150	150
Wavelength [Å]	1.54180	0.71070	0.71070	0.71070
Crystal system, space group	monoclinic, *C*2/*c*	monoclinic, $P2_1/a$	monoclinic, $P2_1/a$	monoclinic, $P2_1/c$
Unit-cell dimensions:				
a [Å]	30.241(2)	17.085(2)	17.769(3)	14.423(3)
b [Å]	10.527(1	16.865(2)	16.302(3)	13.512(3)
c [Å]	29.533(1)	20.077(3)	20.070(1)	25.873(6)
β [Å]	90.671(4)	111.94(1)	111.79(1)	90.76(2)
Volume [Å^3]	9401(1)	5366(1)	5398(1)	5042(2)
Z, D_c [mg/cm^3]	8, 1.629	4, 1.573	4, 1.564	4, 1.678
μ [mm^{-1}]	4.394	0.469	0.466	1.286
F(000)	4576	2544	2544	2520
Crystal size [mm]	0.5×0.5×0.4	0.7×0.5×0.5	0.7×0.6×0.4	0.65×0.5×0.3
θ Range [°]	2.92–57.10	4.11–26.20	3.75–28.77	3.71–26.18
Reflections collected/unique	14129/5856	23678/8842	28673/11801	22950/8197
Data/restraints/parameters	5450/0/641	5696/0/721	5132/0/721	5823/0/458
Goodness-of-fit on F^2	1.033	1.029	0.808	1.411
Final R indices ($I>2\sigma(I)$)	$R_1=0.0666$, $wR_2=0.1751$	$R_1=0.0592$, $wR_2=0.1546$	$R_1=0.0505$, $wR_2=0.1211$	$R_1=0.1368$, $wR_2=0.3629$
R indices (all data)	$R_1=0.0694$, $wR_2=0.1776$	$R_1=0.0895$, $wR_2=0.1712$	$R_1=0.1101$, $wR_2=0.1311$	$R_1=0.1601$, $wR_2=0.3885$

REFERENCES

[1] B. Cornils, W. A. Herrman, 'Applied Homogeneous Catalysis with Organometallic Compounds', VCH, Weinheim, 1996; E. Negishi, A. de Meijere, 'Handbook of Organopalladium Chemistry for Organic Synthesis', Wiley, New York, 2002.

[2] A. Sen, 'Catalytic Synthesis of Alkene–Carbon Monoxide Copolymers and Cooligomers', Kluwer Academic Publishers, Dordrecht, 2003.

[3] a) E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663; b) K. Nozaki, T. Hiyama, *J. Organomet. Chem.* **1999**, *576*, 248; c) C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35.

[4] K. R. Reddy, K. Surekha, G. H. Lee, S. M. Peng, J. T. Chen, S. T. Liu, *Organometallics* **2001**, *20*, 1292 and ref. cit. therein.

[5] F. C. Rix, M. Brookhart, P. S. White, *J. Am. Chem. Soc.* **1996**, *118*, 4746.

[6] P. Margl, T. Ziegler, *J. Am. Chem. Soc.* **1996**, *118*, 7337; M. Svensson, T. Matsubara, K. Morokuma, *Organometallics* **1996**, *15*, 5568.

[7] a) K. Nozaki, H. Komaki, Y. Kawashima, T. Hiyama, T. Matsubara, *J. Am. Chem. Soc.* **2001**, *123*, 534; b) M. Brookhart, F. C. Rix, J. M. DeSimone, J. C. Barborak, *J. Am. Chem. Soc.* **1992**, *114*, 5894.

[8] A. Aeby, F. Bangerter, G. Consiglio, *Helv. Chim. Acta* **1998**, *81*, 764; A. Gsponer, T. M. Schmid, G. Consiglio, *Helv. Chim. Acta* **2001**, *84*, 2986.

[9] K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, N. Koga, *J. Am. Chem. Soc.* **1997**, *119*, 12779.

[10] H. Shen, R. F. Jordan, *Organometallics* **2003**, *22*, 1878.

[11] F. Ozawa, T. Hayashi, H. Koide, A. Yamamoto, *J. Chem. Soc., Chem. Commun.* **1991**, 1469; B. A. Markies, K. A. N. Verkerk, M. H. P. Rietveld, J. Boersma, H. Kooijman, A. L. Spek, G. van Koten, *J.*

Chem. Soc., Chem. Commun. **1993**, 1317; R. van Asselt, E. E. C. G. Gielsens, R. E. Rülke, K. Vrieze, C. J. Elsevier, *J. Am. Chem. Soc.* **1994**, *116*, 977.
[12] G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1992**, *430*, 357.
[13] a) C. Carfagna, G. Gatti, D. Martini, C. Pettinari, *Organometallics* **2001**, *20*, 2175; b) C. Carfagna, M. Formica, G. Gatti, A. Musco, A. Pierleoni, *Chem. Commun.* **1998**, 1113.
[14] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
[15] J. Setsune, T. Yamauchi, S. Tanikawa, Y. Hirose, J. Watanabe, *Organometallics* **2004**, *23*, 6058.
[16] C. Carfagna, G. Gatti, L. Mosca, P. Paoli, A. Guerri, *Organometallics* **2003**, *22*, 3967.
[17] B. Binotti, C. Carfagna, G. Gatti, D. Martini, L. Mosca, C. Pettinari, *Organometallics* **2003**, *22*, 1115.
[18] H. von Schenck, S. Strömberg, K. Zetterberg, M. Ludwig, B. Åkermark, M. Svensson, *Organometallics* **2001**, *20*, 2813.
[19] 'Biosym/MSI', 9685 Scranton Road, San Diego, CQA 92121-3652, USA.
[20] U. C. Singh, P. A. Kollman, *J. Comput. Chem*. **1984**, *5*, 129; B. H. Besler, K. M. Merz Jr., P. A. Kollman, *J. Comput. Chem*. **1990**, *11*, 431.
[21] G. Consiglio, *Chimia* **2001**, *55*, 809.
[22] G. Milano, G. Guerra, M. Mazzeo, C. Pellecchia, L. Cavallo, *Macromolecules* **2005**, *38*, 2072.
[23] 'SMART: Area Detector Integration Software', Siemens Industrial Automation, Inc., Madison, WI, 1995.
[24] 'SAINT Version 4.0', Siemens Industrial Automation, Inc., Madison, WI, 1995.
[25] G. M. Sheldrick, 'SADABS', University of Göttingen, Germany, 1996.
[26] 'CrysAlis CCD', Version 1.171.27p20 beta (release 16-09-2005 CrysAlis171 .NET), compiled Sept 16, 2005, Oxford Diffraction Ltd.
[27] 'CrysAlis RED', Version 1.171.27p20 beta (release 16-09-2005 CrysAlis171 .NET), compiled Sept 16, 2005, Oxford Diffraction Ltd.
[28] 'ABSPACK', Version 1.171.27p20 beta (release 16-09-2005 CrysAlis171 .NET), compiled Sept 16, 2005, Oxford Diffraction Ltd.
[29] A. Altomare, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[30] G. M. Sheldrick, 'SHELX 97', University of Göttingen, Germany, 1997.
[31] G. Gatti, J. A. Lopez, C. Mealli, A. Musco, *J. Organomet. Chem.* **1994**, *483*, 77.
[32] M. Nardelli, *Comput. Chem.* **1983**, *7*, 95.
[33] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, 'Gaussian 03, Revision B05', Gaussian, Inc., Pittsburgh PA, 2003.
[35] R. C. Binning Jr., L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206; L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning Jr., L. Radom, *J. Chem. Phys.* **1995**, *103*, 6104; M. P. McGrath, L. Radom, *J. Chem. Phys.* **1991**, *94*, 511; M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.
[36] C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.* **1996**, *17*, 49.

Received February 17, 2006