Iodination of α-Phosphino Enolate Complexes of Palladium(II) and Platinum(II). Synthesis and Crystal Structures of [(dmba)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] and of the Dipalladium(II) Complex [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(tmeda)] Obtained by Palladium(0) Insertion into the Carbon−Iodine Bond

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Electrophilic attack of 1 equiv of I_2 on a PC_{sp^2} carbon of the Pt(II) complex *cis*-[Pt{$Ph_2PCH\cdots C(\cdots O)Ph$}$_2$] (**1**) afforded *cis*-[Pt(I)[$Ph_2PCH\cdots C(\cdots O)Ph$]{$Ph_2PCH(I)C(O)Ph$}] (**2**) in 90% yield. Complex **2** was subsequently deprotonated by NaOEt in ethanol to give the bis(enolato) complex *cis*-[Pt{$Ph_2PCH\cdots C(\cdots O)Ph$}{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (**3**). This α-phosphino, α-iodo enolato complex was obtained directly and quantitatively by the reaction of **1** with 1 equiv of *N*-iodosuccinimide (NIS). When 2 equiv of NIS was used, the symmetrical complex *cis*-[Pt{$Ph_2PC(I)\cdots C(\cdots O)Ph$}$_2$] (**4**) was formed selectively. In contrast to I_2, NIS was also able to functionalize the phosphino enolate ligand of complexes [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}] to give the corresponding iodo derivatives [(C N)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (C N = dmba (**5**) or 8-mq (**6**)). These represent the first examples in which a phosphino enolate C−H bond has been directly functionalized, i.e. replaced by a C−X bond. Attempts to use this procedure with *cis*-[Ni{$Ph_2PCH\cdots C(\cdots O)Ph$}$_2$] or with [Ni(Ph){$Ph_2PCH\cdots C(\cdots O)Ph$}($PPh_3$)] were unsuccessful. Reaction of **5** with $Pd(dba)_2$ in the presence of tetramethylenediamine (tmeda) or 2,2′-bipyridine (bipy) afforded [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(tmeda)] (**7**) and [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(bipy)] (**8**), respectively. The solid state structures of complexes **5** and **7**·CH_2Cl_2 have been determined by single-crystal X-ray diffraction: **5** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 12.867(3)$ Å, $b = 10.625(3)$ Å, $c = 19.509(6)$ Å, and $\beta = 102.23(2)°$; **7**·CH_2Cl_2 crystallizes in the monoclinic space group $C2/c$ with $Z = 8$ in a unit cell of dimensions $a = 35.906(3)$ Å, $b = 13.565(3)$ Å, $c = 15.775(2)$ Å, and $\beta = 95.099(10)°$. Complex **7** contains two palladium(II) centers, in a square-planar environment, connected by the P−C unit of a phosphino enolate ligand which adopts an unprecedented μ-$\eta^2(P,C)$:$\eta^2(P,O)$ bonding mode. The two coordination planes are almost orthogonal and make a dihedral angle of 88.0(2)°, which minimizes the steric hindrance between the ligands.

Introduction

In the course of our studies on the synthesis and reactivity of mononuclear phosphino enolate complexes of the transition metals, we considered the possibility of using them as precursors for the synthesis of heterometallic, functional complexes. Air-stable, square planar complexes of the type [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)R$}] (C N = cyclometalated dimethylbenzylamine or 8-methylquinoline; R = Ph, OEt, NPh_2) and *cis*-[M{$Ph_2PCH\cdots C(\cdots O)R$}$_2$] (M = Ni, Pd, Pt) are excellent candidates for the study of chemoselective reactions between the enolate moiety and electrophilic reagents, and we have conducted such studies with electrophiles like carbon dioxide, organic nitriles and isocyanates, activated alkynes and chlorophosphines.[1] However, little is known about the reactivity of these phosphino enolate complexes with electrophilic *metal centers*. We have found that complexes of the softer metal ions Pd(II) and Au(I) reacted with formation of a PC_{sp^2}−metal bond, as in [(C N)Pd(μ-Cl){μ-$Ph_2PCHC(O)OEt$}Pd(C N)] (eq 1)[2] or in [(C N)Pd{$Ph_2PCH(AuPPh_3)C(O)Ph$}](BF_4) (eq 2).[3] In contrast, the "harder" Co(II) center in CoI_2 is chelated by the oxygen atoms of the nickel complex *cis*-[Ni{$Ph_2PCH\cdots C(\cdots O)Ph$}$_2$] to give a heterometallic, paramagnetic molecule constituted by two metal complexes (eq 3).[3b]

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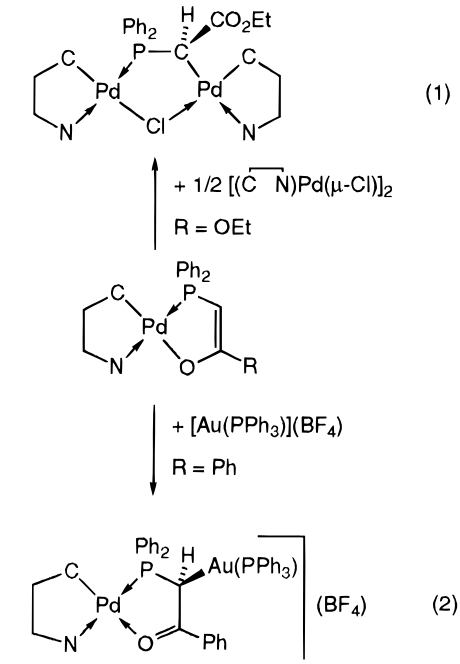
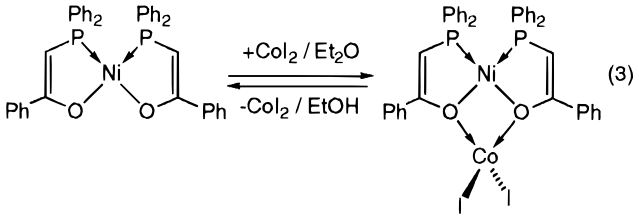
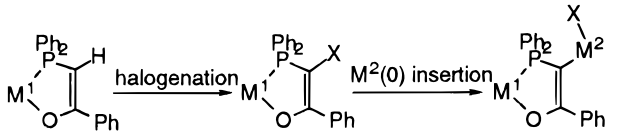




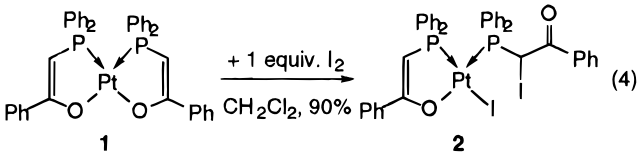
Since the enolato PC−H bond is retained in all these reactions, formation of a bond between the PC_{sp^2} carbon and another carbon or a metal results in the generation of a PC_{sp^3} center. We wondered whether our systems could lead to stable heterometallic metallo enolate complexes, i.e. complexes in which the second metal would be covalently linked to the enolato sp^2 carbon of the precursor molecule. This could open the way to interesting new reactivity. Intermediates containing a Pd−C_{sp^2} bond are involved in numerous transformations, such as Heck-type carbon−carbon coupling reactions with alkynes or alkenes[4] and the synthesis of mixed-valence ruthenium complexes[5] or of organometallic polymers with interesting properties in nonlinear optics.[6] Thus, the question was how to replace the enolato C−H bond with a C−metal bond, and we decided to explore the strategy depicted in Scheme 1. It involves first formation of a carbon−halogen bond that could allow subsequent insertion of a zerovalent metal fragment. This approach does not appear to have been much investigated in the past.

Scheme 1



Results

Reaction of the Pt(II) complex *cis*-[Pt{Ph_2PCH••C(••O)Ph}$_2$] (**1**)[1f] with 1 equiv of iodine in CH_2Cl_2 afforded *cis*-[Pt(I){Ph_2PCH••C(••O)Ph}{Ph_2PCH(I)C(O)Ph}] (**2**) in 90% yield (eq 4). The IR spectrum of **2** shows typical



absorptions at 1507 and 1676 cm^{-1} for the enolate and the keto functions, respectively. The resonances for the P atoms appear at δ 39.1 and −8.4 in the $^{31}P\{^1H\}$ NMR spectrum and show a ^2J(PP) coupling of 10 Hz, typical for a *cis* arrangement. An electrophilic attack of I_2 on the PC_{sp^2} carbon, followed by coordination of the iodide anion to platinum accounts for the formation of **2**.

With the corresponding palladium and nickel complexes, a similar reaction led respectively to decomposition or formation of a red, paramagnetic compound that was not further investigated. In the reaction of Li[Ph_2PCH••C(••O)Ph] with I_2, carried out for comparison, no product could be characterized although iodine oxydation reactions of Li[$Ph_2PCHPPh_2$] and Li[Ph_2PNPPh_2] have recently led to interesting P−P, P−C, C−C, and P−N coupling products.[7] Obviously, the nature of the cation associated with the phosphino enolate ligand strongly influences its reactivity.

Complex **2** was subsequently deprotonated by NaOEt in ethanol to give *cis*-[Pt{Ph_2PCH••C(••O)Ph}{Ph_2PC(I)••C(••O)Ph}] (**3**) (eq 5). Its IR spectrum contains absorptions at 1521 and 1506 cm^{-1} which correspond to the two different

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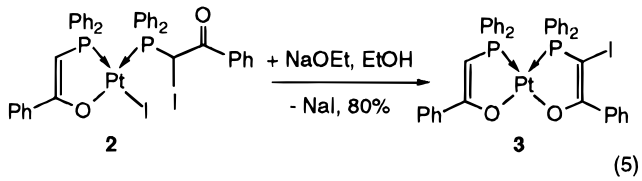
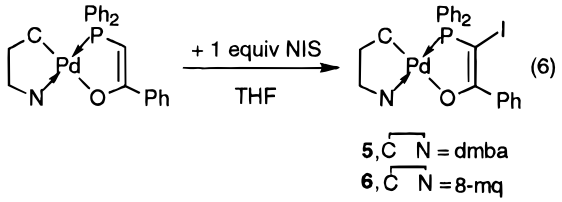


(5)

phosphino enolate ligands. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at δ 27.1 and 13.8 which show a characteristic $^2J(PP)$ cis coupling of 11.8 Hz. Interestingly, complex **3** could be obtained directly and quantitatively by the reaction of **1** with 1 equiv of *N*-iodosuccinimide (NIS). When 2 equiv of NIS was used, the symmetrical complex **4** was formed selectively (Scheme 2). Its $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ 28.0 with a $^1J(Pt-P)$ coupling constant of 3542 Hz, in agreement with a *cis* structure (Scheme 2). The ^1H NMR spectrum of **4** indicates the loss of the PCH proton. The $\nu(C\cdots O) + \nu(C\cdots C)$ absorption of **1** at 1517 cm^{-1} is shifted to 1505 cm^{-1} in **4**, a value similar to one of the two absorptions found in **3**.

In contrast to I_2, NIS is able to functionalize the phosphino enolate ligand of complexes [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}] to give the iodo derivatives [(dmba)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (**5**) and [(8-mq)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (**6**) (eq 6). The succinimide formed is easily removed with water



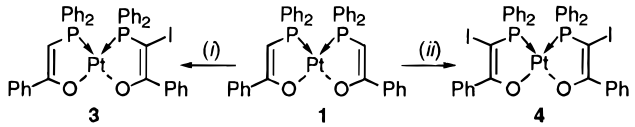
(6)

which does not protonate the enolate carbon atom of complexes **5** or **6**. In the IR spectrum, the $\nu(C\cdots C) + \nu(C\cdots O)$ absorption of **5** and **6** is found at 1495 and 1501 cm^{-1}, respectively. In order to analyze the structural influence of the iodo substituent, an X-ray diffraction study was performed on **5** (see below).

Attempts to extend this procedure to *cis*-[Ni{$Ph_2PCH\cdots C(\cdots O)Ph$}$_2$][1k] or [Ni(Ph){$Ph_2PCH\cdots C(\cdots O)Ph$}($PPh_3$)], the classical SHOP-type catalyst model,[8] were unsuccessful. Broad signals were observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra which suggested the presence of paramagnetic complexes.

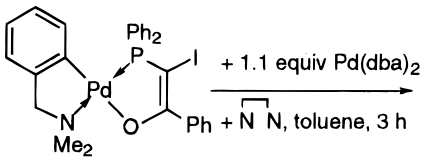
With the aim of exploiting the newly created C−I functionality of **5** or **6** for further coupling reactions, we reacted **5** with HC≡CPh or HC≡CSiMe_3 in the presence of Pd(PPh_3)$_4$ and CuI.[5,9] Since no reaction was observed, we wondered whether this was due to a lack of reactivity of the C−I bond toward Pd(0). Oxidative insertion of the metal catalyst species into the aryl−halogen bond generally represents the rate-determining

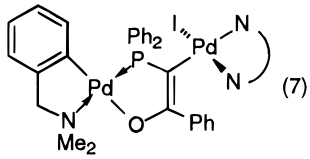
Scheme 2



(*i*) + 1 equiv. NIS, THF, 1 h, 64%. (*ii*) + 2 equiv. NIS, THF, 4 h, 70%

step in the Heck reaction.[4] Indeed, **5** did not react with Pd(PPh_3)$_4$ in toluene at 60 °C. However, the desired reaction took place when nitrogen-containing ligands were coordinated to palladium(0). Thus, reaction of **5** with Pd(dba)$_2$ in the presence of tetramethylenediamine (tmeda) or 2,2′-bipyridine (bipy) afforded [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(tmeda)] (**7**) and [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(bipy)] (**8**), respectively (eq 7). The ^1H NMR spectrum of **7** and **8** shows an ABX-





(7)

type pattern (X = P) for the dmba methylene protons, consistent with the lack of any symmetry element in these molecules. As expected, the IR spectrum contains no absorption due to a coordinated ketone (which would have resulted if the enolate carbon had become sp^3-hybridized) but the enolate absorption was obscured by other strong ligand absorptions around 1490 cm^{-1}. In order to firmly establish the molecular structure of this unusual dinuclear complex, an X-ray diffraction study was performed on a single crystal of **7** (see below).

Whereas the tmeda ligand in *cis*-[Pd(Ph)I(tmeda)] is easily displaced by chelating nitrogen or phosphorus donors,[9a,b] this is not the case with **7**. Thus, no reaction was observed between **7** and 1 equiv of bipy (CH_2Cl_2, 3 h) although the expected product **8** formed directly in the reaction of eq 7. Similarly, **7** did not react with dppe (toluene, 60 °C, 6 h). Obviously, the kinetic inertness of **7** in these reactions must be due to steric factors. The crystal structure determination of **7** (see below) showed that the coordination planes of the two palladium atoms are almost orthogonal (88.0(2)°) and that the phenyl rings C(11)−C(16) at P and C(25)−C(30) at C(24) might generate steric shielding preventing easy attack of a nucleophile at Pd(1) to generate a five-coordinate transition state.

When complex **7** was reacted with the PhC≡CH/NEt_3/CuI system,[10a] only [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}][1f] could be isolated. The hydrogen atom that replaced the palladium σ-bonded to the PC_{sp^2} carbon of **7** originates from the am-

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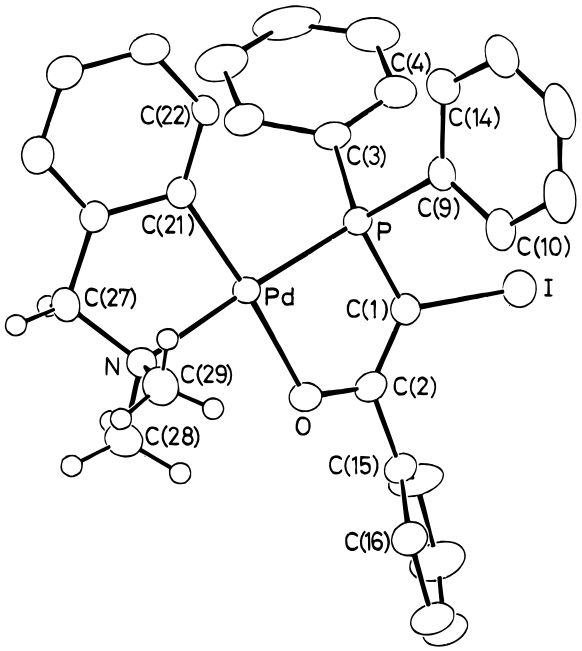


Figure 1. ORTEP view of the molecular structure of [(dmba)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (**5**).

monium salt [$HNEt_3$]I which is formed. This was independently confirmed by the reaction of **7** with 1 equiv of [$HNEt_3$]Cl, which yielded [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}]. The reactivity of the Pd−C_{sp^2} bond of **7** therefore requires the use of aprotic reagents. We also tried to perform C−C coupling reactions in basic media, as described by Cassar or Heck.[10b,c] No reaction was observed between **7** and the sodium phenylacetylide generated *in situ* from PhC≡CH and NaOMe. This lack of reactivity may be ascribed to the steric factors discussed above.

Crystal Structures of [(dmba)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (5) and [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(tmeda)]·$CH_2Cl_2$ (7·CH_2Cl_2). A view of the molecular structure of complex **5** is shown in Figure 1; selected bond distances and angles are given in Table 1. The palladium atom has a square planar environment involving the N and C(21) atoms of the three-electron donor cyclometalated ligand and P and O atoms of the three-electron donor phosphino enolate ligand. The oxygen atom of one five-membered chelate ring is *trans* with respect to the C(21) atom of the other ring. The maximum deviations from the mean plane containing the Pd, P, C(1), C(2), and O atoms are found for palladium (−0.0518(4) Å) and oxygen (0.058(4) Å) and the iodine atom is at a distance of 0.0423(4) Å. The carbon atoms C(1) and C(2) are situated on the same side of the palladium coordination plane, at 0.24(1) and 0.17(2) Å. The dmba chelate has an envelope conformation with C(27) being −0.481(5) Å out of the mean plane passing through the Pd, C(21), C(26), and N atoms. The bond distances to Pd are in the normal range. The dimensions involving the dmba chelate are similar to those determined for this ligand in other Pd(II) complexes.[1e,11] The Pd-O distance of 2.074(3) Å is only slightly shorter than that in [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)OEt$}] (2.117(5) Å)[1b] or in [(dmba)Pd{$Ph_2PCH_2C(O)O$}] (2.105(3) Å).[1e] The C(1)−I distance of 2.099(5) Å corresponds to a C_{sp^2}−I bond and to the sum of the covalent radii of sp^2-carbon (0.74 Å) and iodine (1.33 Å). The C(1)−C(2) and C(2)−O distances of 1.359(6) Å and 1.300(6) Å are fully consistent with their partial double bond character and electron delocalization within the *P,O* chelate.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **5**

Pd−P	2.238(1)	C21−C22	1.341(6)
Pd−O	2.074(3)	C21−C26	1.415(6)
Pd−C21	1.986(4)	C22−C23	1.402(7)
Pd−N	2.135(4)	C23−C24	1.378(8)
I−C1	2.099(5)	C24−C25	1.364(8)
P−C1	1.792(5)	C25−C26	1.392(7)
P−C3	1.810(4)	C26−C27	1.481(7)
P−C9	1.830(5)	N−C27	1.492(6)
C1−C2	1.359(6)	N−C28	1.473(7)
C2−O	1.300(6)	N−C29	1.473(7)
C2−C15	1.489(6)		
P−Pd−O	83.99(9)	Pd−C21−C22	131.0(3)
P−Pd−C21	101.0(1)	Pd−C21−C26	111.8(3)
P−Pd−N	175.1(1)	C22−C21−C26	117.2(4)
O−Pd−C21	174.9(2)	Pd−N−C27	105.0(3)
O−Pd−N	92.0(1)	Pd−N−C28	113.0(3)
C21−Pd−N	83.0(2)	Pd−N−C29	109.4(3)
Pd−P−C1	98.7(1)	C27−N−C28	110.6(4)
Pd−P−C3	117.6(2)	C27−N−C29	109.7(4)
Pd−P−C9	118.2(2)	C28−N−C29	109.1(4)
C1−P−C3	109.7(2)	C26−C27−N	109.8(4)
C1−P−C9	107.1(2)	C1−C2−C15	125.5(4)
C3−P−C9	104.9(2)	O−C2−C15	112.9(4)
I−C1−P	118.7(2)	Pd−O−C2	118.3(3)
I−C1−C2	124.1(3)	C21−C26−C25	120.1(4)
P−C1−C2	116.7(4)	C21−C26−C27	118.3(4)
C1−C2−O	121.6(4)	C25−C26−C27	121.6(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The crystal structure of **7**·CH_2Cl_2 consists of discrete molecular units separated by normal van der Waals contacts and dichloromethane molecules of solvation (Figure 2). Selected bond lengths and angles are listed in Table 2. The molecule contains two palladium(II) centers, in square-planar environments, connected by the P−C unit of a phosphino enolate ligand which adopts an unprecedented μ-η^2(*P,C*):η^2(*P,O*) bonding mode. The two coordination planes are almost orthogonal and make a dihedral angle of 88.0(2)°, which minimizes the steric hindrance between the ligands. The coordination around Pd(2) is very similar to that of the palladium atom in **5** and does not need therefore to be discussed in detail. The atoms C(2) and C(3) are situated on the same side of the Pd(2) coordination plane, at 0.61(1) and 0.35(1) Å, respectively. The slight deformation of the Pd(2) coordination plane manifests itself by the distances of Pd(2) (0.045(2) Å), P (−0.097(3) Å), O (0.082(3) Å), N(1) (−0.107(3) Å), and C(4) (0.076(3) Å) to the mean plane passing through these atoms.

The coordination around Pd(1) is defined by the two nitrogen donors of the chelating tmeda ligand, an iodide ligand and the sp^2-hybridized carbon atom C(23) of the phosphino enolate ligand which chelates Pd(2). This is similar to the situation in Pd(Ph)I(tmeda).[9a,b] The C(23)−Pd(1)−I angle of 89.3(2)° reflects the lack of steric constraint between these ligands. The difference of 0.053 Å between the Pd(1)−N(3) and Pd(1)−N(2) bond distances results from the higher *trans*-influence of the σ-bonded sp^2 C(23) atom.[9c] The Pd(1)−C(23) and Pd(2)−C(4) distances are similar (2.019(7) and 1.997(8) Å, respectively) and the Pd(1)−I distance of 2.596(1) Å, which falls near the

(11) Canty, A. J. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, England, 1995; Vol. 9, Chapter 5, pp 1−72.

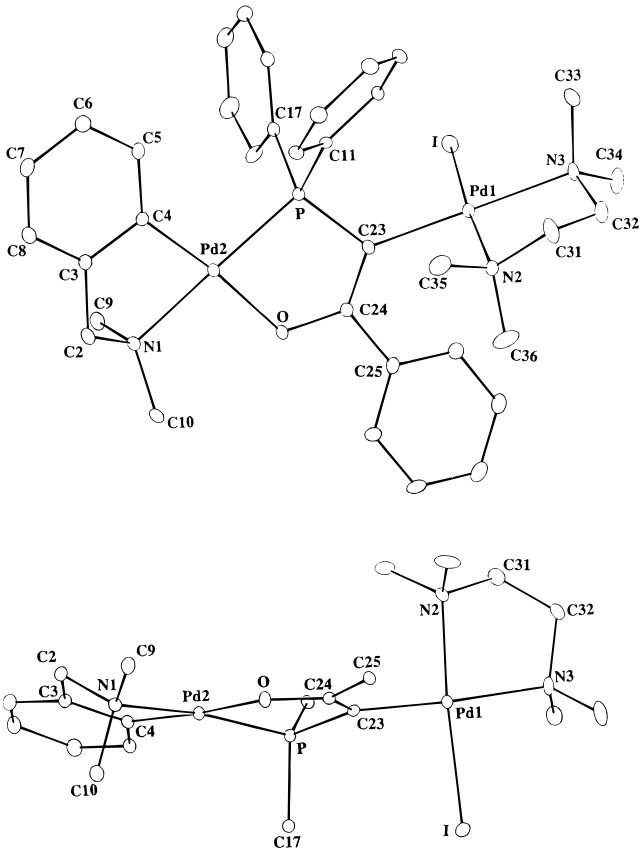


Figure 2. ORTEP view of the molecular structure of [(dmba)Pd{$Ph_2PC\cdots C(\cdots O)Ph$}Pd(I)(tmeda)] in **7**·$CH_2Cl_2$: (a) top view; (b) view showing the almost orthogonal orientation of the metal coordination planes.

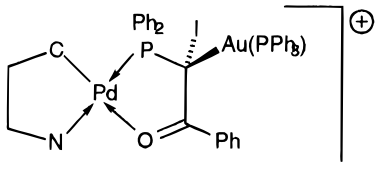
lower quartile (2.593 Å) for this bond in the sample of 15 structures analyzed in 1989,[12] is longer than that in Pd(Ph)I(tmeda) (2.5703(8) Å).[9a,b] Whereas the enolate C(23)−C(24) bond of 1.356(11) Å has the same length as the corresponding C(1)−C(2) bond in **5** (1.359(6) Å), consistent with a strong double bond character, the C(24)−O bond of 1.344(9) Å is slightly longer than that in **5** (1.300(6) Å).

Discussion

α-Phosphino, α-iodo enolate ligands are conveniently obtained by the reaction of palladium or platinum complexes containing the M[$Ph_2PCH\cdots C(\cdots O)Ph$] (M = Pd, Pt) moiety with *N*-iodosuccinimide. These represent the first examples in which the phosphino enolate C−H bond has been directly functionalized, i.e. replaced by a C−X bond. With complexes containing two chelating phosphino enolate ligands, the reaction can be controled by stoichiometry which allows introduction of the C−I bond in only one or in both chelates (Scheme 2). Complex **3** was also prepared by the reaction of **2** with NaOEt in EtOH, the latter complex being obtained by iodine addition to **1**. The formation of C−I and Pt−I bonds in the reaction of eq 4 illustrates the heterolytic I^+/I^- behavior of iodine.

Reaction of the palladium complexes [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}] (C N = dmba, 8-mq) with 1 equiv of NIS occurred selectively at the C_{sp^2} carbon of the phosphino enolate ligand to give **5** and **6**, respectively. These complexes are air-stable and are not hydrolized by H_2O. The failure to observe a Pd/Cu-catalyzed coupling with terminal alkynes is not due to the inability of the C−I bond to react with the Pd(0) catalyst, although the nature of the ligands coordinated to Pd(0) plays a key role. This was shown by the reaction of eq 7 which required the presence of nitrogen donor ligands, such as tmeda or bipy, instead of phosphines. Complexes **7** and **8** were obtained under experimental conditions similar to those used to prepare *cis*-[Pd(Ph)I(tmeda)] from $Pd(dba)_2$, tmeda, and Ph−I,[9a,b] indicating a similar reactivity of the C−I bond in **5** and in phenyl iodide.

Note that by analogy with the protonation reaction which converts **7** into [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}], the reaction of the isolobal cation $[Au(PPh_3)]^+$ with **5** (felt to be less reactive than **7** or **8** and therefore a better candidate) led to decomposition of the addition product. We confidently assign structure **A** to this intermediate by analogy with that of the



(**A**)

structurally characterized Pd−Au complex [(8-mq)Pd{Ph_2PCH-($AuPPh_3$)-C(O)Ph}](BF_4).[3b] The geminal arrangement of the bulky iodide and $Au(PPh_3)$ substituents is obviously too destabilizing.

In previous studies on phosphino enolate complexes of the d^8 metals, which led to addition reactions at the enolate carbon (CO_2, activated alkynes, organic nitriles and isocyanates, [Au(PPh_3)]$^+$, [Pd(μ-Cl)(C N)]$_2$) or at the enolate oxygen (chlorophosphines, CoI_2), the phosphino enolate ligand behaved as a 3- or 5-electron donor.[1] (Note also the situation in the

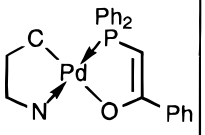
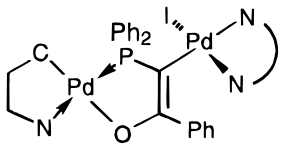
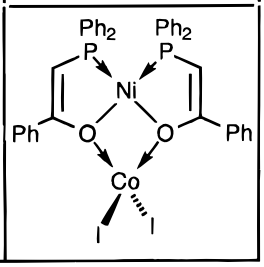
Table 2. Selected Bond Lengths (Å) and angles (deg) for **7**·CH_2Cl_2

Pd(1)−C(23)	2.019(7)	P−C(17)	1.830(8)
Pd(1)−I	2.5963(9)	Pd(2)−C(4)	1.997(8)
Pd(1)−N(2)	2.159(7)	Pd(2)−N(1)	2.145(6)
N(2)−C(31)	1.459(12)	N(1)−C(2)	1.494(11)
N(2)−C(35)	1.452(13)	N(1)−C(9)	1.478(11)
N(2)−C(36)	1.427(12)	N(1)−C(10)	1.470(11)
Pd(1)−N(3)	2.212(7)	C(2)−C(3)	1.483(12)
N(3)−C(32)	1.475(13)	C(3)−C(4)	1.418(11)
N(3)−C(33)	1.461(13)	Pd(2)−O	2.068(6)
N(3)−C(34)	1.45(2)	O−C(24)	1.344(9)
Pd(2)−P	2.228(2)	C(23)−C(24)	1.356(11)
P−C(23)	1.795(8)	C(24)−C(25)	1.507(11)
P−C(11)	1.824(7)	C(31)−C(32)	1.39(2)

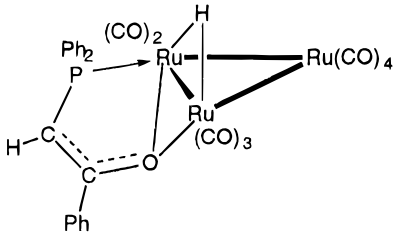
C(23)−Pd(1)−N(2)	94.4(3)	C(31)−N(2)−Pd(1)	104.0(6)
C(23)−Pd(1)−N(3)	176.1(3)	C(32)−N(3)−Pd(1)	104.8(6)
N(2)−Pd(1)−N(3)	82.8(3)	C(24)−O−Pd(2)	117.2(5)
C(23)−Pd(1)−I	89.3(2)	C(3)−C(2)−N(1)	108.8(7)
N(2)−Pd(1)−I	175.4(2)	C(4)−C(3)−C(2)	118.7(8)
N(3)−Pd(1)−I	93.7(2)	C(3)−C(4)−Pd(2)	111.8(6)
C(4)−Pd(2)−O	174.1(3)	C(24)−C(23)−P	111.6(6)
C(4)−Pd(2)−N(1)	82.4(3)	C(24)−C(23)−Pd(1)	128.0(6)
O−Pd(2)−N(1)	92.2(2)	P−C(23)−Pd(1)	120.3(4)
C(4)−Pd(2)−P	103.0(2)	O−C(24)−C(23)	124.6(8)
O−Pd(2)−P	82.6(2)	C(23)−C(24)−C(25)	125.3(8)
N(1)−Pd(2)−P	170.6(2)		
C(23)−P−Pd(2)	102.5(3)		
C(2)−N(1)−Pd(2)	105.6(5)		

(12) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Scheme 3. Bonding Modes for the Phosphino Enolate *P,O* Ligand in Metal Complexes

P,O chelate	3e donor	4e donor	5e donor
formal charge	-1	-2	-1
in complexes			

Ru_3clustershown below where this ligand behaves as a 5-electron donor μ-η^1(O):η^2(*P*,*O*) ligand[13]).



In the present work for the first time, the enolate C−H proton has been replaced by a functional group (iodine) which allows the synthesis of a new type of dinuclear complexes in which the phosphino enolate behaves as a 4-electron donor dianionic ligand. These various situations are schematically presented below (Scheme 3).

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC 300 instrument. IR spectra were recorded in the 4000−400 cm^{-1} range on a Bruker IFS66 FT spectrometer.

B. Syntheses. The complexes Pd(dba)$_2$ (dba = dibenzylideneacetone),[14] *cis*-[M{$Ph_2PCH\cdots C(\cdots O)Ph}_2$] (M = Ni, Pd, Pt) and [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}] (C N) = dmba, 8-mq) were prepared according to procedures reported previously.[1k]

***cis*-[Pt(I){$Ph_2PCH\cdots C(\cdots O)Ph$}{$Ph_2PCH(I)C(O)Ph$}] (2).** A solution of I_2 (0.215 g, 0.830 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of complex **1** (0.663 g, 0.827 mmol) in CH_2Cl_2 (20 mL). The yellow solution was filtered and concentrated to two-thirds its original volume. Addition of pentane afforded yellow crystals of **2** (0.785 g, 90%), mp > 160 °C dec. IR (KBr): ν(CO) 1676 vs, ν(C$\cdots$C) + ν(C$\cdots$O) 1507 s. ^{1}H NMR ($CDCl_3$): δ 8.18−6.82 (m, 31 H, aromatic + P^{1}CH(I)), 4.81 (d, with Pt satellites, 1 H, P^{2}CH, ^2J(PH) = 10.7 Hz, ^3J(PtH) = 25.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 39.1 (d with Pt satellites, 1 P, ^2J(PP) = 10 Hz, ^1J(PtP) = 3454 Hz), −8.4 (d with Pt satellites, 1 P, ^2J(PP) = 10 Hz, ^1J(PtP) = 3591 Hz). Anal. Calcd for $C_{40}H_{32}I_2O_2P_2Pt$ (*M* = 1055.53): C, 45.52; H, 3.06. Found: C, 45.27; H, 3.00.

***cis*-[Pt{$Ph_2PCH\cdots C(\cdots O)Ph$}{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (3).**

Method 1. A solution of NaOEt (prepared from 0.20 g of Na) in EtOH (10 mL) was added to a solution of complex **2** (0.208 g, 0.224 mmol) in EtOH (20 mL). After being stirred for 1 h, the solution was filtered and the solvent was removed *in vacuo*. The white residue was washed with EtOH (10 mL) and dried *in vacuo*. Recrystallization from CH_2Cl_2/pentane afforded white needles of **3**·0.5CH_2Cl_2 (0.166 g, 80%), mp > 210 °C. IR (KBr): ν(C$\cdots$C) + ν(C$\cdots$O) 1521 s, 1506 s. ^{1}H NMR ($CDCl_3$): δ 7.96−7.03 (m, 30 H, aromatic), 4.80 (d with Pt satellites, 1 H, PCH, ^2J(PH) = 7.0 Hz, ^3J(PtH) = 30.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.1 (d with Pt satellites, 1 P, ^2J(PP) = 11.8 Hz, ^1J(PtP) = 3495 Hz), 13.8 (d with Pt satellites, 1 P, ^2J(PP) = 11.8 Hz, ^1J(PtP) = 3552 Hz). Anal. Calcd for $C_{40}H_{31}IO_2P_2Pt$·0.5 CH_2Cl_2 (*M* = 927.61 + 42.46): C, 50.14; H, 3.32. Found: C, 49.85; H, 3.45.

Method 2. A solution of *N*-iodosuccinimide (0.055 g, 0.244 mmol) in THF (5 mL) was added to a solution of complex **1** (0.191 g, 0.238 mmol) in THF (20 mL). After being stirred for 1 h, the solvent was removed *in vacuo*. The residue was washed several times with water (10 mL) in order to remove the succinimide formed and dried *in vacuo*. Recrystallization from CH_2Cl_2/pentane afforded white needles of complex **3** (0.160 g, 70%).

***cis*-[Pt{$Ph_2PC(I)\cdots C(\cdots O)Ph$}$_2$] (4).** A solution of *N*-iodosuccinimide (0.078 g, 0.354 mmol) in THF (5 mL) was added to a solution of complex **1** (0.131 g, 0.163 mmol) in THF (10 mL). After being stirred for 4 h, the solvent was removed *in vacuo*. The residue was washed several times with water (10 mL). The product was recrystallized from THF/pentane and white crystals of **4** were obtained (0.110 g, 64%), mp > 180−190 °C dec. IR (KBr): ν(C$\cdots$C) + ν(C$\cdots$O) 1505 s. ^{1}H NMR ($CDCl_3$): δ 7.65−7.05 (m, 30 H, aromatic). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 28.0 (s with Pt satellites, ^1J(PtP) = 3542 Hz). Anal. Calcd for $C_{40}H_{30}I_2O_2P_2Pt$ (*M* = 1053.52): C, 45.60; H, 2.87. Found: C, 45.65; H, 2.87.

[(dmba)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (5). A solution of *N*-iodosuccinimide (0.208 g, 0.924 mmol) in THF (10 mL) was added to a solution of [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)Ph$}] (0.500 g, 0.919 mmol) in THF (20 mL). After being stirred for 2 h, the solvent was removed *in vacuo*. The residue was washed several times with water and dried *in vacuo*. Recrystallization from CH_2Cl_2/pentane afforded yellow-orange crystals of **5**·CH_2Cl_2, which were suitable for X-ray diffraction analysis (0.380 g, 62%), mp >200 °C dec. IR (KBr): ν(C$\cdots$C) + ν(C$\cdots$O) 1495 s. ^{1}H NMR ($CDCl_3$): δ 6.60−7.99 (m, 19 H, aromatic), 3.95 (d, 2H, CH_2N, ^4J(PH) = 1.5 Hz), 2.85 (d, 6 H, Me_2N, ^4J(PH) = 2.2 Hz). ^{31}P{^{1}H} NMR (THF/C_6D_6): δ 49.0 (s). Anal. Calcd for $C_{29}H_{27}INOPPd$·CH_2Cl_2 (*M* = 669.84 + 84.93): C, 47.74; H, 3.87; N, 1.86. Found: C, 47.85; H, 3.63; N, 1.83.

Reaction of 5 with AuCl(PPh$_3$). Solid $AgBF_4$ (0.060 g, 0.306 mmol) was added to a stirred solution of AuCl(PPh_3) (0.150 g, 0.303 mmol) in THF (30 mL) and the mixture stirred for 0.5 h. It was filtered, and the filtrate was added to complex **5** (0.230 g, 0.305 mmol) in THF (10 mL). After the mixture was stirred for 1 h, the solvent was removed under reduced pressure. A white solid was obtained which slowly decomposed to palladium metal. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.1 [d, 1 P, AuP, ^3J(PP) = 10.0 Hz], 63.4 [d, 1 P, PdP, ^3J(PP) = 10.0 Hz].

[(8-mq)Pd{$Ph_2PC(I)\cdots C(\cdots O)Ph$}] (6). A solution of *N*-iodosuccinimide (0.125 g, 0.553 mmol) in THF (10 mL) was added to a

(13) Braunstein, P.; Coco Cea, S.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *423*, C38.

(14) (a) Ito, T.; Takahashi, Y.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 629. (b) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169.

Table 3. Crystal Data and Data Collection for **5** and **7**·CH_2Cl_2

mol formula	$C_{29}H_{27}NOPIPd$	$C_{35}H_{43}IN_3OPPd_2{\cdot}CH_2Cl_2$
fw	669.6	977
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a, *b*, *c* (Å)	12.867 (3), 10.625 (3), 19.509 (6)	35.906 (3), 13.565 (3), 15.775 (2)
β (deg)	102.23 (2)	95.099 (10)
V (Å^3); Z; ρ_{calcd} (g cm^{-3})	2606 (1); 4; 1.707	7653 (2); 8; 1.655
F (000); linear abs coeff (cm^{-1})	1320; 19.8	3872; 19.5
radiation (graphite monochromator)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
no. of data collcd	3232	13665
no. of unique data used, *N*	2798 [$I > 6\sigma(I)$]	4182 [$I > 2\sigma(I)$]
$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.029	0.046
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.034	0.068
weighting scheme	$1.000/[\sigma^2(F) + 0.002941F^2]$	$1.000/[\sigma^2(F) + (0.0146P)^2 + 71.33P]$ $P = (\max(F_0^2,O) + 2F_c^2)/3$
largest shift/esd, final cycle	2.04 (U_{12} C(22))	0.43 (U_{22} C(31))
GOF = $[\sum w(\|F_o\| - \|F_c\|)^2/(N_{observn} - N_{params})]^{1/2}$	0.82	1.21

solution of [(8-mq)Pd{$Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)Ph$}] (0.300 g, 0.543 mmol) in THF (20 mL). After being stirred for 8 h, the solvent was removed *in vacuo*. The residue was washed several times with water (20 mL) and dried *in vacuo*. The product was recrystallized from CH_2Cl_2/pentane, affording orange crystals of **6** (0.185 g, 55%), mp > 200 °C dec. IR (KBr): ν(C$\cdot\cdot$C) + ν(C$\cdot\cdot$O) 1501 s. ^{1}H NMR ($CDCl_3$): δ 8.30−7.25 (m, 21 H, aromatic), 3.10 (d, 2 H, CH_2Pd, ^3J(PH) = 1.3 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.8 (s). Anal. Calcd for $C_{30}H_{23}INOPPd$ (M = 677.82): C, 53.16; H, 3.42; N, 2.07. Found: C, 53.15; H, 3.33; N, 2.09.

[(dmba)Pd{$Ph_2PC{\cdot\cdot}C({\cdot\cdot}O)Ph$}Pd(I)(tmeda)] (7). To a mixture of **5**·CH_2Cl_2 (0.250 g, 0.331 mmol) and $Pd(dba)_2$ (0.250 g, 0.364 mmol) was added toluene (30 mL) and the ligand tmeda (0.6 mL, 0.397 mmol). The dark red solution was stirred at 40−45 °C for 3 h, and a red suspension was obtained. The solvent was removed *in vacuo*. The red residue was washed several times with Et_2O (3 × 20 mL), dried in vacuo, redissolved in CH_2Cl_2 and filtered. Addition of pentane afforded red crystals which were suitable for X-ray diffraction analysis (0.296 g, 76%). IR (CH_2Cl_2): 1578 m, 1490 w, 1478 m, 1460 vs. ^{1}H NMR (CD_2Cl_2): δ 9.0−6.6 (m, 19 H, aromatic), 4.20 (d, 1 H, CH^AN, A part of an ABX spin system for CH^AH^BNPd, ^2J(AB) = 13.8 Hz, ^4J(AX) < 2 Hz), 3.63 (dd, 1 H, CH^BN, B part of an ABX spin system for CH^AH^B-NPd, ^2J(AB) = 13.8 Hz, ^4J(BX) = 2.2 Hz), 3.00 (d, 3 H, Me^AN of Me^AMe^BNPd, ^4J(PH) = 2.2 Hz), 2.70 (d, 3 H, Me^BN of Me^AMe^BNPd, ^4J(PH) = 1.6 Hz), 2.61 (s, 3 H, Me^AN of tmeda), 2.56 (s, 3 H, Me^BN of tmeda), 2.35−1.86 (m, 4 H, $N(CH_2)_2N$ of tmeda), 1.56 (s, 3 H, $Me^{A\prime}N$ of tmeda), 1.37 (s, 3 H, $Me^{B\prime}N$ of tmeda). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 56.3 (s). Anal. Calcd for $C_{35}H_{43}IN_3OPPd_2{\cdot}CH_2Cl_2$ (M = 892.47 + 84.93): C, 44.24; H, 4.64; N, 4.30. Found: C, 44.33; H, 4.59; N, 4.32.

[(dmba)Pd{$Ph_2PC{\cdot\cdot}C({\cdot\cdot}O)Ph$}Pd(I)(bipy)] (8). This complex was prepared by the same procedure as **7**, starting from **5** (0.105 g, 0.157 mmol), $Pd(dba)_2$ (0.089 g, 0.173 mmol) and solid bipy (0.027 g, 0.173 mmol); yield (0.095 g, 59%). IR (CH_2Cl_2): 1577 m, 1566 w, 1491 w, 1470 m, 1468 vs. ^{1}H NMR (CD_2Cl_2): δ 9.6−6.5 (m, 27 H, aromatic), 4.07 (d, 1 H, CH^AN, A part of an AB spin system for CH^AH^B-NPd, ^2J(AB) = 13.9 Hz), 3.94 (d, 1 H, CH^BN, B part of an AB spin system for CH^AH^BNPd, ^2J(AB) = 13.9 Hz), 3.00 (d, 3 H, Me^AN of Me^AMe^BNPd, ^4J(PH) = 1.9 Hz), 2.90 (d, 3 H, Me^BN of Me^AMe^BNPd, ^4J(PH) = 1.8 Hz), $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.3 (s). Anal. Calcd for $C_{39}H_{35}IN_3OPPd_2{\cdot}CH_2Cl_2$ (M = 932.45): C, 50.24; H, 3.78; N, 4.51. Found: C, 49.97; H, 4.04; N, 4.42.

Crystal Structure Determinations for Compounds 5 and **7**·CH_2Cl_2. The crystallographic data for both compounds are summarized in Table 3. Data were collected at room temperature (25 °C) on an Enraf Nonius CAD4 diffractometer (compound **5**) and on a Siemens diffractometer equiped with an area charge coupled device detector (for **7**·CH_2Cl_2). The data reductions were performed respectively with the Enraf-Nonius SDP/VAX package[15] and with the program SMART (Siemens Molecular Analysis Research Tool).[16] Intensities were corrected for Lorentz and polarization effects and a morphology-based absorption correction was applied.[17] Partial structures were solved using the Patterson methods of SHELXS[18] (compound **5**) or direct methods of phases determination of SHELXL[19] (for **7**·CH_2Cl_2). Successive Fourier methods allowed the determination of the positions of the heavy atoms and refinement was done by full-matrix least-squares methods with anisotropic thermal parameters. All hydrogen atoms (excepting those of the CH_2Cl_2 molecule) were placed at their geometrically calculated positions and refined (for **5**), with fixed C−H distances taking into account the hybridization of the carbon atom (for **7**·CH_2Cl_2). Their thermal parameters were fixed. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 20.

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Supporting Information Available: Tables giving complete crystallographic experimental details (Table S-I), atomic coordinates of the non-hydrogen atoms (Tables S-II (**5**) and S-III (**7**·CH_2Cl_2)), atomic coordinates of the hydrogen atoms (Tables S-IV (**5**) and S-V (**7**·CH_2Cl_2)), anisotropic thermal parameters (Tables S-VI (**5**) and S-VII (**7**·CH_2Cl_2)), and complete bond distances and angles (Tables S-VIII (**5**) and S-IX (**7**·CH_2Cl_2)) (18 pages). Ordering information is given on any current masthead page.

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