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Complexes with Functional Phosphines. 14.[1a] Coupling Reactions of $MeO_2CC{\equiv}CCO_2Me$ with *β*-Phosphino Ketonate Complexes Leading to Nickel, Palladium, and Platinum Alkenyl Complexes

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Alkenyl complexes of formula [M{Ph$_2$PCH[C(O)Ph][(MeO$_2$C)C=C(CO$_2$Me)]}$_2$] (**2**, M = Ni; **4**, M = Pd; **7**, M = Pt) have been prepared by the reaction of dimethyl acetylenedicarboxylate (DMAD) with the phosphino enolato complexes *cis*-[M{Ph$_2$PCH=C(O)Ph$_2$}$_2$] (**1**, M = Ni; **3**, M = Pd; **5**, M = Pt). The tendency to form trans products decreases on going from nickel to platinum. The molecular structure of the diastereomer *u-trans*-**4** has been determined by X-ray analysis. Compound *u-trans*-**4** crystallizes in the monoclinic space group *C*2/*c* with *a* = 20.961 (3) Å, *b* = 11.445 (4) Å, *c* = 39.359 (4) Å, and *β* = 101.27 (1)°. The Pd–C alkenyl bond lengths are 2.081 (7) and 2.061 (7) Å. Whereas the double coupling reaction with the Ni– and Pd–enolato complexes (**1** and **3**, respectively) occurs at room temperature, that with the Pt analogue **5** has to be performed in refluxing THF. However, reaction of **5** with DMAD in refluxing CH$_2$Cl$_2$ leads to coupling with only one phosphino enolate ligand: *cis*-[Pt{Ph$_2$PCH=C(O)Ph}{Ph$_2$PCH[C(O)Ph][(MeO$_2$C)C=C(CO$_2$Me)]}] (**6**). Isomerization reactions of the new phosphino alkenyl ligands were shown to occur in both complexes [(*o*-C$_6$H$_4$CH$_2$NMe$_2$)Pd{Ph$_2$PCH[C(O)Ph][(MeO$_2$C)C=C(CO$_2$Me)]}] (**12**) and **7**: thus, refluxing a THF solution of **12** for 24 h gave the P,O-chelate complex [(*o*-C$_6$H$_4$CH$_2$NMe$_2$)Pd{Ph$_2$PC[=C(O)Ph][(MeO$_2$C)C=C(H)(CO$_2$Me)]}] (**13**), whereas heating a toluene solution of **7** diastereoselectively led to the bis(alkyl) complex *l-cis*-[Pt{Ph$_2$PC[C(O)Ph)]=C(MeO$_2$C)CH(CO$_2$Me)}$_2$] (**8**). The solid-state structure of **8** was determined by X-ray crystallography. Compound **8** crystallizes in the monoclinic space group *C*2/*c* with *a* = 22.750 (7) Å, *b* = 13.281 (3) Å, *c* = 17.420 (9) Å, and *β* = 102.95 (3)°. The platinum atom is in a nearly square-planar environment, and the CO$_2$Me groups of the metalated carbon atoms are situated on each side of the metal plane. The Pt–C bond lengths are 2.108 (8) Å. Reaction of DMAD with [Ni(Ph)(PPh$_3$){Ph$_2$PCH=C(O)Ph}] afforded regioselectively the insertion product into the Ni–Ph bond [Ni{(Ph)(MeO$_2$C)C=C(CO$_2$Me)}(PPh$_3$){Ph$_2$PCH=C(O)Ph}] (**10**), and no coupling with the enolate moiety was observed.

Introduction

It is well-known that functional phosphine ligands R$_2$P∼Z are able to enhance the chemical reactivity of transition-metal complexes or induce selective pathways whenever, in the course of a reaction, bonding interactions occur between the metal or the substrate and the functional group(s) Z.[2] Complexes containing functional phosphines that act as *dissymmetric* chelating ligands have been shown to possess drastically different properties (e.g., selectivity control) to those observed for similar complexes containing symmetrical ligands.[3] It has also been established that, in some complexes, the chelating behavior of such functional phosphines is not permanent.[4] In particular, the functional group may easily dissociate from the metal center in solution if competition occurs with an incoming substrate or a solvent molecule; these hemilabile ligands may therefore be used for the stabilization and storage of catalyst precursors or of reactive species.[5] In other complexes the chelating ligand may react with a substrate molecule and lead to a new ligand capable of modifying the molecular properties of the complex.[6] When this ligand-centered coupling reaction is reversible, which may be achieved by a fine-tuning of the metal–ligand interactions, the subsequent transfer of the (pre)activated substrate may be performed.[6c] In principle, such

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[1] (a) For Part 13 see: Balegroune, F.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 3320. (b) The configurational notation used in this work is that of: Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

[2] See, for example: (a) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395. (b) Caplar, V.; Comisso, G.; Sunjic, V. *Synthesis* **1981**, 85. (c) Brown, J. M. *Platinum Met. Rev.* **1987**, *31*, 137 and references cited therein. (d) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1986**, *312*, C37. (e) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941.

[3] (a) Behr, A.; Freudenberg, U.; Keim, W. *J. Mol. Catal.* **1986**, *35*, 9. (b) Agbossou, S.; Bonnet, M. C.; Tkatchenko, I. *Nouv. J. Chim.* **1985**, *5*, 311.

[4] (a) Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Carluer, B.; Grandjean, D.; Lemoine, P. *J. Chem. Soc., Dalton Trans.* **1986**, 415. (b) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *J. Organomet. Chem.* **1989**, *367*, 117.

[5] Lindner, E.; Meyer, S. *J. Organomet. Chem.* **1988**, *339*, 193.

[6] (a) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279. (b) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *J. Chem. Soc., Chem. Commun.* **1987**, 488. (c) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.

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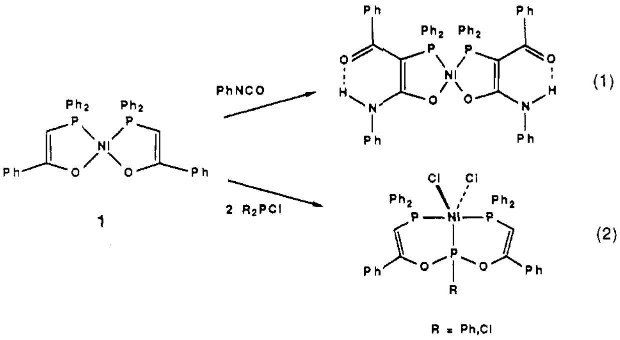
Scheme I

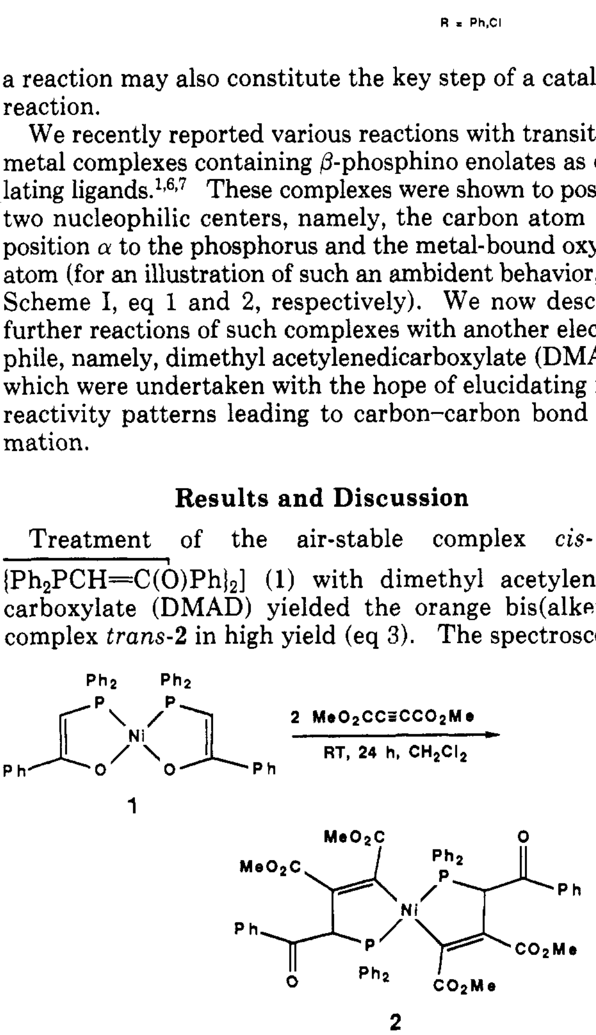


a reaction may also constitute the key step of a catalytic reaction.

We recently reported various reactions with transition-metal complexes containing β-phosphino enolates as chelating ligands.[1,6,7] These complexes were shown to possess two nucleophilic centers, namely, the carbon atom in a position α to the phosphorus and the metal-bound oxygen atom (for an illustration of such an ambident behavior, see Scheme I, eq 1 and 2, respectively). We now describe further reactions of such complexes with another electrophile, namely, dimethyl acetylenedicarboxylate (DMAD), which were undertaken with the hope of elucidating new reactivity patterns leading to carbon–carbon bond formation.

Results and Discussion

Treatment of the air-stable complex *cis*-[$\overline{\text{Ni}\{Ph_2PCH{=}C(O)Ph\}_2}$] (1) with dimethyl acetylenedicarboxylate (DMAD) yielded the orange bis(alkenyl) complex *trans*-2 in high yield (eq 3). The spectroscopic properties of this and other new complexes are given in the Experimental Section. The carbon–carbon coupling reactions leading to *trans*-2 generate two chiral carbon atoms, and this complex thus exists as two diastereomers (*trans*-2a and *trans*-2b), formed in a 90:10 ratio during the reaction. Complex *trans*-2 is thermally stable and is recovered after prolonged heating at 100 °C in toluene. Furthermore, the complex thus formed does not react with excess of DMAD nor with ethylene at 90 °C (30 bar, toluene) to give, e.g., further C–C coupling products. When the reaction of eq 3 was followed by ^1H NMR, small amounts of other unidentified products were detected besides *trans*-2. None of these could be isolated, but diastereomers having a cis structure are likely to be formed. It was independently verified that pure 1 does not rearrange to the trans isomer upon standing in dichloromethane solution for days, suggesting that *cis*-2 would be the kinetic product. The reaction of eq 3 confirms our previous observations that complex 1 behaves as a stabilized double carbanion capable of nucleophilic attack on unsaturated substrates.[6] However, other alkynes (HC≡CH, EtC≡CCO$_2$Me, PhC≡CPh, or F$_3$CC≡CCF$_3$) were found to be unreactive toward 1 under similar conditions.



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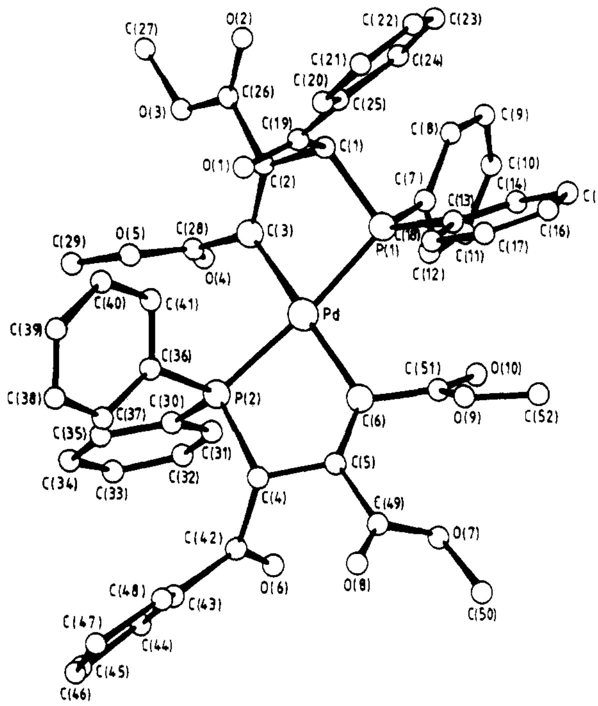
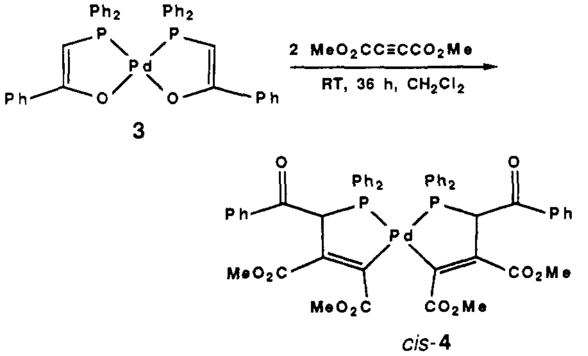


Figure 1. ORTEP drawing of *u-trans*-[$\overline{\text{Pd}\{Ph_2PCH[C(O)Ph]-[(MeO_2C)C{=}C}(CO_2Me)]\}_2$] (*u-trans*-4).

Reaction of the palladium complex 3 with DMAD is slower than with the nickel analogue. It is only after ca. 36 h at room temperature that the reaction was complete, and the bis insertion product *cis*-4 was isolated as a mixture of two diastereomers, *l*-*cis*-4 and *u*-*cis*-4,[1b] which could be separated by fractional crystallization (eq 4). The structure of the diastereomer *u*-*cis*-4 was determined by a single-crystal X-ray analysis and has been detailed



(4)

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(7) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(8) (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *17*, 466. (b) Keim, W. *Nouv. J. Chim.* **1987**, *11*, 531.

(9) As a second reaction step, a reductive elimination with coupling between the [Ph$_2$PCH=C(O)Ph] ligand and the first formed, nickel-bound, [(Ph)(MeO$_2$C)C=C(CO$_2$Me)] fragment are also envisagable. See relevant work by: Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987** *334*, 141.

(10) (a) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kürschner, V.; Limbäcker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356. (b) Behr, A.; Keim, W.; Thelen, G. *J. Organomet. Chem.* **1983**, *249*, C38.

(11) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

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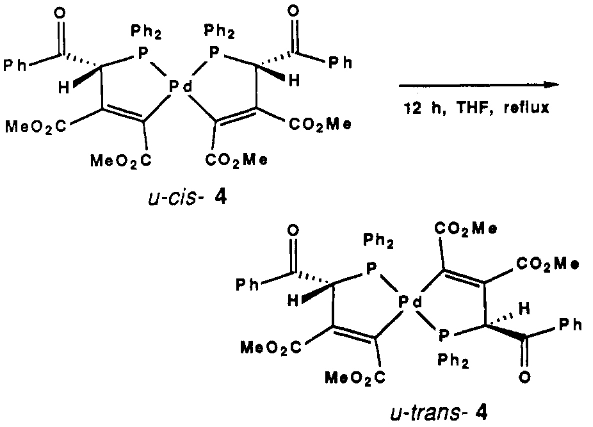
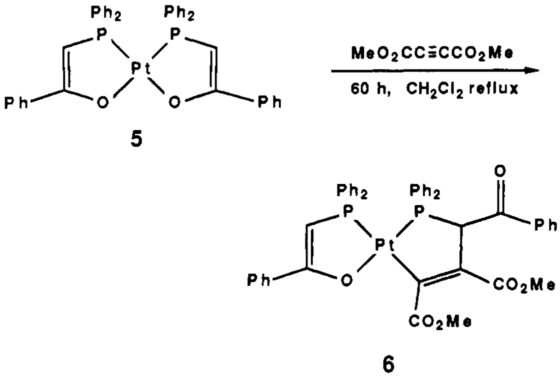
elsewhere.[13] By heating a solution of *u-cis*-4, isomerization occurred and the thermodynamically more stable product having a trans P–Pd–P arrangement was formed quantitatively (eq 5). The molecular structure of *u-trans*-4 is



(5)

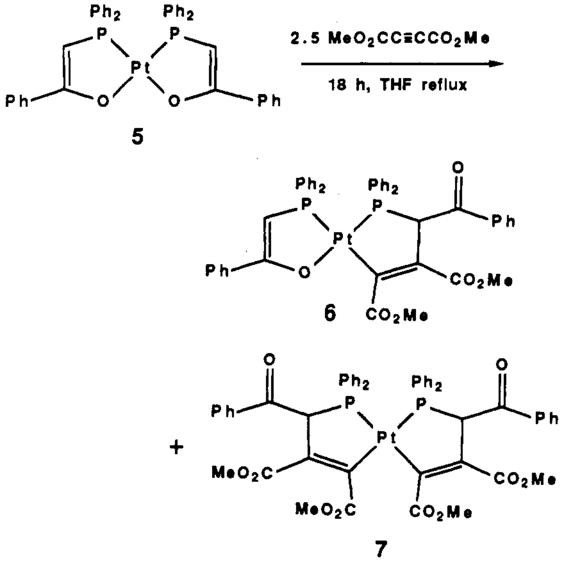
shown in Figure 1 and is discussed below. We checked by NMR that no cis–trans isomerization had occurred within the 15 min following the addition at room temperature of small amounts of pyridine as promoter to a $CDCl_3$ solution of *u-cis*-4.

In order to evaluate the influence of the metal center on the reactivity of the phosphino enolate ligand, we also investigated the reaction of the platinum complex 5 with DMAD. In contrast to 1 and 3, complex 5 does not react with DMAD at room temperature. However, upon refluxing 5 and DMAD in CH_2Cl_2 for 60 h, the coupling product 6 was formed quantitatively (eq 6). When the

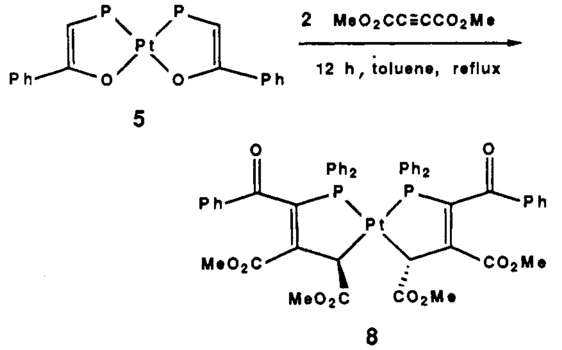


(6)

reaction was performed in refluxing THF, the product of double coupling 7, analogous to *cis*-4, was formed (yield ca. 25% after a 24-h reaction time) in addition to significant amounts of 6 (eq 7). As for 2 and 4, complex 7 was obtained as a mixture of two diastereomers that may be separated (see Experimental Section). The relative difficulty in forming 7 parallels the diminished reactivity already observed for 5 vs 1 and 3 toward aryl isocyanates to yield C–C coupling products[6] and further exemplifies the key role that the metal ion exerts on the reactivity of its coordination sphere.

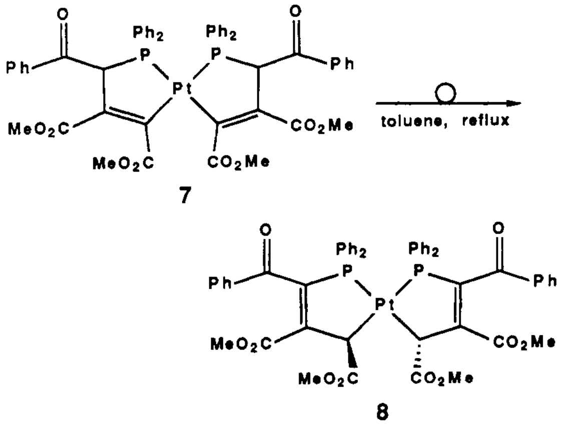


(7)



(8)

With the hope of obtaining 7 quantitatively, we also investigated the reaction of 5 with 2 equiv of DMAD in *refluxing toluene*. A bis-coupling reaction indeed occurred, however, to yield 8, an isomer of 7 resulting from a 1,3-H shift (eq 8). This complex of *l* configuration was formed diastereoselectively (see below). It contains two chiral carbon atoms σ-bonded to the metal. The latter point could be unambiguously deduced from the ^{13}C NMR ($\delta(C_{Pt})$ 52.80 ppm, $J(C–Pt) = 480$ Hz, $^2J(C–P_{trans}) = 78$ Hz) and ^1H NMR data ($\delta(H_{CPt})$ 4.88 ppm, $^2J(HPt) = 94$ Hz) and was confirmed by a single-crystal X-ray analysis described below. The formation of complex 8 is likely to proceed via complex 7, as verified by heating of a toluene solution of 7 which resulted in the expected prototropic rearrangement and quantitative formation of 8 (eq 9).



(9)

The higher stability of 8 vs 7 must be due to the stabilization resulting from conjugation within the ligand system since $Pt–C_{sp^3}$ bonds are anticipated to be weaker than $Pt–C_{sp^2}$ bonds.

In view of the fact that $[\overline{Ni(Ph)(PPh_3)\{Ph_2PCH{=}C(O)}Ph\}]$ (9) is a well-known ethylene oligomerization catalyst,[8] it was particularly interesting to compare its re-

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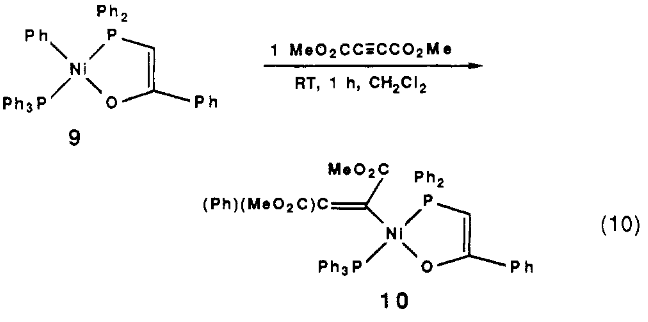
[13] Balegroune, F.; Braunstein, P.; Gomes Carneiro, T. M.; Grandjean, D.; Matt, D. *J. Chem. Soc., Chem. Commun.* **1989**, in press.

Table I. Crystal Data and Data Collection for *u-trans*-4 and *l-cis*-8

	u-trans-4	*l-cis*-8
formula	$C_{52}H_{44}O_{10}P_2Pd$	$C_{52}H_{44}O_{10}P_2Pt\cdot 0.5CH_2Cl_2$
fw	997.28	1128.41
cryst syst	monoclinic	monoclinic
space group	$C2/c$, No. 15	$C2/c$, No. 15
a, Å	20.961 (3)	22.750 (7)
b, Å	11.445 (4)	13.281 (3)
c, Å	39.359 (4)	17.420 (9)
β, deg	101.27 (1)	102.95 (3)
V, Å^3	9260.7	5129
Z	8	4
ρ_{calcd}, g/cm^3	1.430	1.461
cryst dimens, mm	0.25 × 0.30 × 0.15	0.32 × 0.25 × 0.12
$F(000)$	4096	2344
systematic absences	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$ ($h = 2n + 1$); $0k0$ ($k = 2n + 1$)	hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$ ($n \neq 2n$); $0k0$ ($k \neq 2n$)
diffractometer	Nonius CAD-4	Nonius CAD-4
radiatn (graphite monochromator)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
linear abs coeff, cm^{-1}	5.192	29.294
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range, deg	1 + 0.35 tan θ	1 + 0.35 tan θ
θ limits, deg	1–25	1–25
octants collected	($+h,+k,\pm l$)	($\pm h,+k,+l$)
no. of data collected	8255	5181
no. of unique data used	3872 ($F_o^2 \geq 3\sigma(F_o^2)$)	2893 ($F_o^2 \geq 4\sigma(F_o^2)$)
no. of variables	587	301
decay, %	<1	<1
$R_{int} = \sum(F_o^2 - \langle F_o^2\rangle)/\sum F_o^2$	0.090	0.042
$R = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.042	0.049
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.058	0.063
GOF = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/N_{observ} - N_{param}]^{1/2}$	1.521	1.761
largest shift/esd, final cycle	0.250	0.05
largest peak, e/Å^3	0.203	0.849
p factor	0.05	0.05

activity toward acetylenic compounds with that of the related nickel complex 1. Two conceivable reactions of 9 with DMAD were carbon–carbon coupling involving the $[Ph_2PCH{=}C(O)Ph]$ ligand, as shown above, or insertion into the Ni—Ph bond, which in the case of $H_2C{=}CH_2$ is the key step affording, after β-elimination, the Ni—H bond responsible for the catalytic activity.[9] It turned out that the reaction of eq 10 is a fast, quantitative, and regioselective insertion of DMAD into the Ni–Ph bond and not into the enolate ligand. This result is in agreement with those reported by Keim, Behr, et al. about reactions of complex 9 with other unsaturated compounds (diphenylacetylene, carbon dioxide) where selective insertion into the Ni–Ph bond was found to occur.[10]



9

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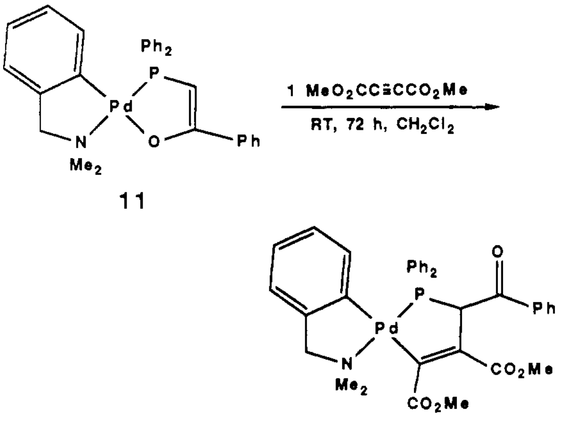
(10)

We also compared the reactivity of complex 9 with that of the structurally related complex $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH{=}C(O)Ph\}]$ (11)[11] in which the Pd–aryl bond is part of a five-membered cyclometallated ring. This complex reacts slowly at room temperature with DMAD affording after a 72-h reaction time complete conversion to complex 12 (eq 11). The "inert" character of the metal–aryl bond of this complex contrasts with that observed in other cyclopalladated complexes of dimethylbenzylamine and could be accounted for by the inability of DMAD to occupy a position cis with respect to the Pd–aryl bond, a prerequisite for such an insertion reaction to take place.[12] The fact that a coupling reaction occurs with the P,O ligand may be related to the weak Pd–O bond which allows labilization of the oxygen atom and therefore facilitates nucleophilic attack of the carbon, in a position α to the phosphorus atom, on the activated alkyne. This explanation appears reasonable although the detailed mechanism of the C–C bond formation in this type of reaction remains unknown.



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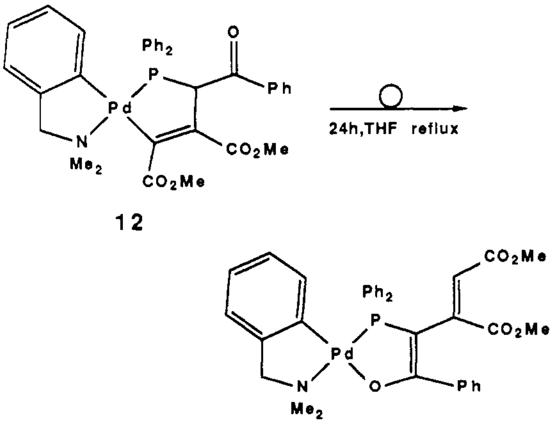
(11)

When complex 12 was heated in refluxing THF (eq 12), isomerization occurred, leading to complex 13 which contains a fully conjugated phosphine ligand system. The structure of this complex was determined by a single-crystal X-ray analysis and has been detailed elsewhere.[13] This reaction implies a Pd–C bond dissociation as well as a H migration from the chiral carbon atom of 12 to the metallated alkenyl carbon atom and ligand rotation about the P–C bond. The phosphine ligand of complex 13 represents the third type of three-electron donor ligand which could be obtained by reaction of coordinated $[Ph_2PCH{=}C(O)Ph]^-$ with DMAD. An isomerization similar to that of eq 12 has been found to be reversible in the complexes resulting from reaction of aryl isocyanates with 11.[6]



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13

(12)

Table II. Selected Interatomic Distances (Å) and Angles (deg) in *u-trans*-4

Bond Distances			
Pd-P(1)	2.287 (2)	P(2)-C(4)	1.877 (8)
Pd-P(2)	2.287 (2)	P(2)-C(30)	1.807 (8)
Pd-C(3)	2.081 (7)	P(2)-C(36)	1.807 (8)
Pd-C(6)	2.061 (7)	C(1)-C(2)	1.51 (4)
P(1)-C(1)	1.865 (7)	C(4)-C(5)	1.52 (1)
P(1)-C(7)	1.807 (7)	C(2)-C(3)	1.34 (1)
P(1)-C(13)	1.804 (8)	C(5)-C(6)	1.34 (1)
Bond Angles			
P(1)-Pd-C(3)	78.5 (2)	P(2)-C(4)-C(5)	106.6 (5)
P(2)-Pd-C(6)	82.5 (2)	C(1)-C(2)-C(3)	120.1 (6)
P(1)-Pd-C(6)	100.5 (2)	C(4)-C(5)-C(6)	123.3 (7)
P(2)-Pd-C(3)	99.3 (2)	C(2)-C(3)-Pd	120.8 (5)
P(1)-C(1)-C(2)	101.8 (5)	C(5)-C(6)-Pd	122.3 (6)

Table III. Selected Interatomic Distances (Å) and Angles (deg) in *l-cis*-8

Bond Distances			
Pt-P(1)	2.248 (2)	C(1)-C(2)	1.31 (1)
Pt-C(3)	2.112 (8)	C(2)-C(3)	1.51 (1)
P(1)-C(1)	1.835 (8)	C(1)-C(16)	1.49 (1)
P(1)-C(4)	1.810 (8)	C(16)-O(1)	1.203 (9)
P(1)-C(10)	1.793 (8)	C(16)-C(17)	1.47 (1)
Bond Angles			
P(1)-Pt-C(3)	84.1 (1)	C(3)-Pt-C′(3)	89.8 (2)
Pt-P(1)-C(1)	103.7 (3)	P(1)-Pt-P′(1)	102.48 (6)
P(1)-C(1)-C(2)	113.2 (6)	P(1)-C(1)-C(16)	121.5 (7)
C(1)-C(2)-C(3)	124.1 (8)	C(1)-C(16)-O(1)	118.8 (7)
C(2)-C(3)-Pt	113.6 (6)		

Structure of *u-trans*-4. An ORTEP view of the structure of this complex is shown in Figure 1, crystal data are given in Table I, and selected interatomic distances and angles in Table II. Selected least-squares planes are presented in Table S-IV (supplementary material). This complex contains two chiral carbon atoms with identical substituents of opposite configuration (i.e. *R* and *S*) but is overall achiral. The palladium atom is in a slightly distorted square-planar environment (the maximum deviation out of its mean coordination plane is 0.155 Å for P(1), and the bite angles of the chelates are close to 80°, see Table II). The phosphorus atoms occupy trans positions, and the bond distances around the palladium atom are normal and fall in the expected range. Note that the Pd-P distances (2.287 (2) Å) and the Pd-C(3) and Pd-C(6) distances (2.081 (7) and 2.061 (7) Å, respectively) are very close to those found in the corresponding complex *cis*-4 (2.278 (2) Å and 2.095 (9) and 2.097 (9) Å, respectively).[13] This could be taken as an indication that the phosphorus donor and the palladium-bound alkenyl groups have a comparable trans influence in these complexes. The newly formed C(1)-C(2) and C(4)-C(5) bonds and the C(2)-C(3) and C(5)-C(6) double bonds are in the expected range for C_{sp^3}-C_{sp^2} and C_{sp^2}-C_{sp^2} distances, respectively.

Structure of *l-cis*-[Pt{Ph$_2$PC[C(O)Ph]=C(MeO$_2$C)CH(CO$_2$Me)}$_2$] (8). An ORTEP view of the molecular structure of complex 8 is shown in Figure 2, crystal data are given in Table I, and selected interatomic distances and angles are presented in Table III. Selected least square planes are available as supplementary material (Table S-IX). This molecule possesses a C_2 symmetry axis relating the primed and non-primed atoms. The platinum atom is in a nearly square planar environment and there are no exceptional bond distances or angles within the chelate rings (see Table III). This structural determination confirmed that 8 is an isomerization product of 7. This is clearly shown by the C(1)=C(2) (1.32 (1) Å) and C(2)—C(3) (1.51 (1) Å) bond distances. The sp^3-carbon atoms attached to platinum have the same stereochemistry, i.e. *R,R* or *S,S*, and since the unit cell contains a center of symmetry, both enantiomers are present. The two CO$_2$Me groups closest to the metal atom are respectively on each side of the metal plane. In such a diastereomer the steric repulsions are obviously minimized.

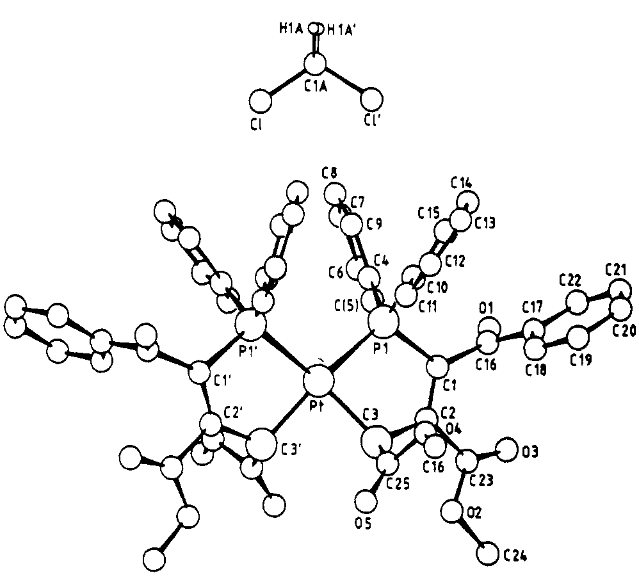
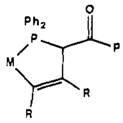


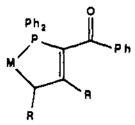
Figure 2. ORTEP drawing of *l-cis*-[Pt{Ph$_2$PC[C(O)Ph]=C(CO$_2$Me)CH(CO$_2$Me)}$_2$] (*l-cis*-8).

Conclusion

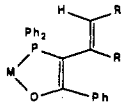
In conclusion, phosphino enolate complexes of the type *cis*-[M{Ph$_2$PCH=C(O)Ph}$_2$] (1, M = Ni; 3, M = Pd; 5, M = Pt) and [(*o*-C$_6$H$_4$CH$_2$NMe$_2$)Pd{Ph$_2$PCH=C(O)Ph}][11] react with DMAD to afford selectively products resulting from carbon–carbon coupling between the enolate fragment(s) and the alkyne triple bond. The reaction rate decreases in the order Ni > Pd > Pt, and the tendency to from trans products from 1, 3, or 5 follows the same sequence. In contrast to the classical methods used to generate metal–alkenyl bonds by alkyne insertion into, e.g., M–C or M–H bonds, the reactions presented in eq 3–7 involve a carbon atom not directly bonded to the metal center. In this study we have also found that three isomeric structures, namely, A–C, of the new polyfunctional ligands may be stabilized.



A



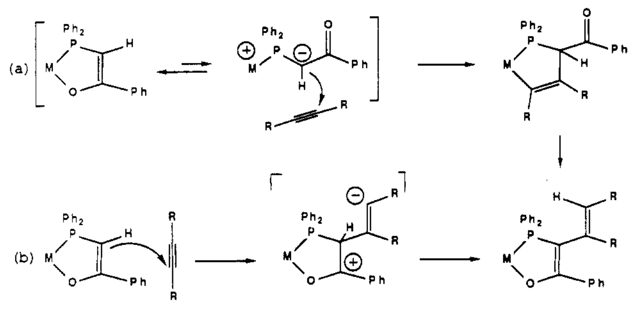
B



C

In all cases studied, the first step of the reaction appears to be the formation of a A-type ligand. This is reminiscent of previous observations about the reactions of similar phosphino enolato complexes with heterocumulenes such as CO$_2$ or ArNCO.[6,7] In the latter cases, however, immediate H shift occurred, generating a P-C_{sp^2} carbon atom. Type A complexes may be thermally isomerized to forms B and C. Bearing in mind that all the isomers needed for a rigorous comparison are not available, the thermodynamically favored ligand arrangement is found to be metal dependent, A for M = Ni, B for M = Pd, and C for M = Pt. Possible sequences of events accounting for the for-

Scheme II



mation of the complexes isolated in the course of this work are displayed in Scheme II. Whether or not the C–C coupling step requires M–O bond dissociation (pathway a or b) cannot be stated at this stage, and further studies on phosphino enolate complexes are in progress.

Experimental Section

All reactions were performed in Schlenk-type flasks under purified nitrogen, using previously detailed procedures.[6,7] The solvents were distilled under nitrogen and dried prior to use. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 200.1 and 81.1 MHz, respectively, on a FT Bruker WP-200 SY instrument, and ^{13}C{^{1}H} NMR spectra were recorded at 100.6 MHz on a FT Bruker AM 400 instrument. ^{1}H and ^{13}C chemical shifts are given relative to external $SiMe_4$ and those for ^{31}P relative to external H_3PO_4. A positive sign denotes a shift downfield to the reference. Dimethyl acetylenedicarboxylate (DMAD) (*caution*: DMAD is a corrosive lachrymator) was purchased from Aldrich, degassed, and used without purification. The complexes [M{$Ph_2PCH{=}C(O)Ph$}$_2$][11] (with M = Ni (1), Pd (3), Pt (5), [(o-$C_6H_4CH_2NMe_2$)Pd{$Ph_2PCH{=}C(O)Ph$}] (11),[11] [Ni(Ph)(PPh_3){$Ph_2PCH{=}C(O)Ph$}] (9)[8] were prepared according to literature methods.

Preparation of *trans*-[Ni{$Ph_2PCH[C(O)Ph][(MeO_2C)C{=}C(CO_2Me)]$}$_2$] (2). A mixture of [Ni{$Ph_2PCH{=}C(O)Ph$}$_2$] (1) (0.300 g, 0.45 mmol) and DMAD (0.120 g, 0.84 mmol) in CH_2Cl_2 (10 mL) was stirred for 24 h. The reaction mixture was evaporated to dryness and the residue washed with pentane. The ^{1}H NMR spectrum of the crude product showed the presence of two diastereomers, **2a** and **2b** present in a 90:10 ratio, which were separated by recrystallization from a mixture of toluene–CH_2Cl_2/hexane. Air stable, orange crystals of **2a** precipitated first. **2a**: yield 0.365 g, 85%; mp 209–210 °C; infrared data (KBr) 1690 br s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 6 H, Me), 3.37 (s, 6 H, Me), 6.10 (virtual t, 2 H, PCH, ^{2+4}J(PH) = 6.9 Hz), 7.12–8.05 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 64.1 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 50.0 (s, Me), 51.6 (s, Me), 63.9 (t, PCH, ^{1+3}J = 28.3 Hz), 163.0 (t, tentative assignment $NiCCO_2$, ^3J(PC) = 6.6 Hz), 174.9 (s, $CHCCO_2$), 177.5 (t, NiC, ^2J(PC) = 19.1 Hz), 196.2 (s, C(O)Ph). Anal. Calcd for $C_{52}H_{44}O_{10}P_2Ni$ (M = 949.55): C, 65.78; H, 4.67. Found: C, 65.00; H, 4.85. Complex **2b** was obtained as a pale yellow powder, always contaminated by **2a**. **2b**: ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 6 H, Me), 3.46 (s, 6 H, Me), 5.97 (virtual t, 2 H, PCH, ^{2+4}J(PH) ~ 8 Hz), ca. 7–8 (aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 64.0 (s).

Preparation of *cis*-[Pd{$Ph_2PCH[C(O)Ph][(MeO_2C)C{=}C(CO_2Me)]$}$_2$] (*cis*-4). A mixture of *cis*-[Pd{$Ph_2PCH{=}C(O)Ph$}$_2$] (0.180 g, 0.25 mmol) and DMAD (0.072 g, 0.51 mmol) in CH_2Cl_2 (10 mL) was stirred for 36 h. The reaction mixture was then filtered and concentrated, and addition of pentane afforded a pale yellow, air-stable powder which was washed with pentane in order to remove free DMAD. The ^{1}H NMR spectrum of the crude product showed the presence of two diastereomers, *u-cis*-**4** and *l-cis*-**4**, present in a 3:1 ratio, which were separated by recrystallization from CH_2Cl_2/pentane. Air-stable, pale yellow crystals of *u-cis*-**4** precipitated first. These were collected and dried in vacuo: yield 0.165 g, 66%; mp >200 °C; infrared data (KBr) 1696 br s cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 6 H, Me), 3.82 (s, 6 H, Me), 5.99 (filled-in d, 2 H, PCH, ^2J(PH) = 12.4 Hz), 6.94–7.70 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 51.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 51.4 (s, Me), 52.0 (s, Me), 62.0 (AXX′ spin system, P*C*, ^{1+3}J(PC) = 31.7 Hz), 164.5 (t, not assigned), 173.9 (s, not assigned), 177.0 (dd, tentative assignment PdC, ^2J(PC) = 122.7, 11.5 Hz), 195.2 (s, *C*(O)Ph). Anal. Calcd for $C_{52}H_{44}O_{10}P_2Pd$ (M = 997.28): C, 62.63; H, 4.44. Found: C, 62.44; H, 4.51. Complex *l-cis*-4 (yellow crystals) was always contaminated by *u-cis*-4. *l-cis*-4: ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 6 H, Me), 3.79 (s, 6 H, Me), 5.83 (filled-in d, 2 H, PCH, ^2J(PH) = 13.5 Hz); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 52.3 (s).

Preparation of *u-trans*-[Pd{$Ph_2PCH[C(O)Ph][(MeO_2C)C{=}C(CO_2Me)]$}$_2$] (*u-trans*-4). A solution of *u-cis*-4 (0.150 g, 0.15 mmol) in THF (10 mL) was refluxed for 12 h. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/pentane affording air-stable, pale yellow crystals of *u-trans*-4: yield 0.140 g, 93%; mp >200 °C; infrared data (KBr) 1707 br s, 1681 br s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 6 H, Me), 3.48 (s, 6 H, Me), 6.26 (virtual t, 2 H, PCH, ^{2+4}J(PH) = 9.4 Hz), 7.18–7.69 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 53.0 (s). Anal. Calcd for $C_{52}H_{44}O_{10}P_2Pd$ (M = 997.28): C, 62.6; H, 4.44. Found: C, 62.83; H, 4.50.

Preparation of *cis*-[Pt{$Ph_2PCH{=}C(O)Ph$}{$Ph_2PCH[C(O)Ph][(MeO_2C)C{=}C(CO_2Me)]$}] (6). A solution of *cis*-[Pt{$Ph_2PCH{=}C(O)Ph$}$_2$] (**5**) (0.400 g, 0.50 mmol) and DMAD (0.071 g, 0.50 mmol) in CH_2Cl_2 (15 mL) was refluxed for 60 h. It was filtered and concentrated, and pentane was added, affording a powder that was washed with pentane in order to remove unreacted DMAD. Recrystallization from CH_2Cl_2/pentane afforded air-stable, pale yellow crystals of **6**. These were collected and dried in vacuo: yield 0.400 g, 85%; mp >200 °C; infrared data (KBr) 1670 br s, 1575 m, 1514 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 3 H, Me), 3.96 (s, 3 H, Me), 4.96 (dd with Pt satellites, 1 H, HC=CPh, J(PH) = 1.1 Hz and 3.7 Hz, ^3J(PtH) ~ 14 Hz), 5.96 (dd with Pt satellites, 1 H, $HCCCO_2$, ^2J(PH) = 12.4 Hz, ^4J(PH) = 1.1 Hz, ^3J(PtH) ~ 25 Hz), 6.69–8.02 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 25.2 (d with Pt satellites, P trans to O, ^2J(PP) ~ 11 Hz, ^1J(PtP) = 3739 Hz), 30.3 (d with Pt satellites, P trans to C, ^2J(PP) ~ 11 Hz, ^1J(PtP) = 2109 Hz). Anal. Calcd for $C_{46}H_{38}O_6P_2Pt$ (M = 943.84): C, 58.54; H, 4.06. Found: C, 58.37; H, 4.20.

Preparation of *cis*-[Pt{$Ph_2PCH[C(O)Ph][(MeO_2C)C{=}C(CO_2Me)]$}$_2$] (7). A solution of *cis*-[Pt{$Ph_2PCH{=}C(O)Ph$}$_2$] (**5**) (1.000 g, 1.25 mmol) and DMAD (0.350 g, 2.5 mmol) in THF (25 mL) was refluxed for 18 h. The solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, and pentane was added affording a precipitate that was filtered off and washed several times with pentane in order to remove the excess of DMAD. The ^{1}H NMR spectrum of this precipitate showed the presence of two diastereomers (yield ca. 25%), **7a** and **7b**, present in a ca. 50:50 ratio and that of **6** (75%). The product was then dissolved in CH_2Cl_2, and pentane was added to the filtered solution, affording first colorless, air-stable crystals (mp >200 °C) of **7a**: yield 0.140 g, 10%; mp >200 °C; infrared data (KBr) 1710 br s cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 6 H, Me), 3.87 (s, 6 H, Me), 5.90 (filled-in d, 2 H, PCH, ^2J(PH) = 12.0 Hz), 6.91–7.64 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6) δ 45.4 (s with Pt satellites, J(PtP) = 2185 Hz). Anal. Calcd for $C_{52}H_{44}O_{10}P_2Pt{\cdot}0.5CH_2Cl_2$ (M = 1128.41): C, 55.61; H, 4.02. Found: C, 55.70; H, 4.02. Complex **7b** was always contaminated by **7a**. **7b**: ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 6 H, Me), 3.87 (s, 6 H, Me), 5.76 (filled-in d, 2 H, PCH, ^2J(PH) ≈ 12 Hz), ca. 6.9–7.6 (30 H, aromatic H); ^{31}P{^{1}H} (CH_2Cl_2/C_6D_6) δ 45.2 (s with Pt satellites), J(PPt) = 2172 Hz).

Preparation of *l-cis*-[Pt{$Ph_2PC[C(O)Ph]{=}C(CO_2Me)CH(CO_2Me)$}$_2$] (8). A suspension of *cis*-[Pt{$Ph_2PCH{=}C(O)Ph$}$_2$] (**5**) (0.400 g, 0.50 mmol) in toluene (20 mL) was refluxed for 12 h in the presence of DMAD (0.142 g, 1.00 mmol). The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/pentane affording air-stable, colorless crystals of **8**; yield

0.149 g, 90%; infrared data (KBr) 1726 s, 1714 sh, 1701 s, 1666 s, 1608 m, 1592 sh cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.47 (s, 6 H, Me), 3.72 (s, 6 H, Me), 4.88 (d with ^{195}Pt satellites, 2 H, PtCH, ^3J(PH) = 6.8 Hz, ^2J(Pt–H) = 84 Hz), 6.70–7.41 (30 H, aromatic H); ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$) δ 47.0 (s, with ^{195}Pt satellites, J(PPt) = 2369 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 51.23 (s, Me), 52.59 (s, Me), 52.80 (d, with ^{195}Pt satellites, CPt, ^2J(CP$_{trans}$) = 78 Hz, J(C^{195}Pt) = 493 Hz), 193.84 (t, *C*(O)Ph, ^3J(C^{195}Pt) = 28 Hz). Other peaks not assigned. Anal. Calcd for $C_{52}H_{44}O_{10}P_2Pd\cdot 0.5CH_2Cl_2$ (M = 1128.41): C, 55.88; H, 4.02. Found: C, 55.48; H, 3.94.

Preparation of $[\overline{\mathrm{Ni}\{(Ph)(MeO_2C)C{=}C(CO_2Me)\}(PPh_3)\{Ph_2PCH{=}C(O}\mathrm{)Ph\}]}$ (10). A solution of DMAD (0.182 g, 1.28 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of **9** (0.900 g, 1.28 mmol in CH$_2$Cl$_2$ (10 mL). Instantaneously, the color turned from yellow to red. After being stirred for 1 h, the solution was filtered over Celite and concentrated, and pentane was added to precipitate a yellow powder. The latter was recrystallized from a mixture of CH$_2$Cl$_2$–toluene/pentane, affording yellow crystals: yield 0.970 g, 89%; mp 208–209 °C; infrared data (KBr) 1734 s, 1709 s, 1691 s cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.78 (s, 3 H, Me), 3.53 (s, 3 H, Me), 4.93 (virtual t, 1 H, PCH, ^{2+4}J(PH) = 2.2 Hz), 6.86–7.94 (35 H, aromatic H); ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$) δ 20.5, 23.1 (AB spin system with ^2J(PP) = 260 Hz; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 49.98 (s, Me), 51.24 (s, Me), 78.36 (d, PCH, J(PC) = 53 Hz), 181.18 (dd, C(O)Ph, J(PC) = 10 and 20 Hz). From the nondecoupled ^{13}C spectrum, J(C$_{\alpha\text{-}P}$H) = 165 Hz). Other peaks not assigned. Anal. Calcd for $C_{50}H_{42}O_5P_2Ni$ (M = 843.52): C, 71.20; H, 5.02. Found: C, 71.16; H, 4.80.

Preparation of $[(o\text{-}\underline{C_6H_4CH_2NMe_2)}\overline{\mathrm{Pd}\{Ph_2PCH[C(O)\text{-}Ph][(MeO_2C)C{=}}\mathrm{C(CO_2Me)]\}]}$ (12). A mixture of $[(o\text{-}\underline{C_6H_4CH_2NMe_2)}\overline{\mathrm{Pd}\{Ph_2PCH{=}C(O}\mathrm{)Ph\}]}$ (**11**) (0.137 g, 0.25 mmol) and DMAD (0.036 g, 0.25 mmol) was stirred in CH$_2$Cl$_2$ (10 mL) for 72 h. The solution was filtered and concentrated, and hexane was added, affording a powder which was washed with hexane. Recrystallization from CH$_2$Cl$_2$/hexane gave pale yellow crystals of **12**. These were collected and dried in vacuo: yield 0.140 g, 82%; mp >200 °C; infrared data (KBr) 1704 m, sh, 1668 s br; ^{1}H NMR (CDCl$_3$) δ 2.68 (d, 3 H, NMe, ^4J(PH) ~ 1.5 Hz), 2.99 (d, 3 H, NMe, ^3J(PH) ~ 3.0 Hz), 3.54 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.63 (H^A), 4.51 (H^B) (ABX spin system (with X = P), 2 H, CH$_2$N, ^3J(PH^A) = 3.3 Hz, ^3J(PH^B) = 0 Hz, J(H^{A}H^B) = 13.6 Hz), 5.99 (d, 1 H, PCH, ^2J(PH) = 13.4 Hz), 6.45–8.10 (19 H, aromatic H); ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$) δ 61.4 (s); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 49.0 (s, Me), 50.8 (s, Me), 51.0 (s, Me), 51.7 (s, Me), 62.8 (d, PCH, J(PC) = 32 Hz), 76.1 (d, NCH$_2$, ^3J(PC) = 2 Hz), 196.3 (s, *C*(O)Ph). Anal. Calcd for $C_{35}H_{34}NO_5PPd\cdot 0.25CH_2Cl_2$ (M = 707.28): C, 59.86; H, 4.92; N, 1.98. Found: C, 60.43; H, 5.04; N, 1.96.

Preparation of $[(o\text{-}\underline{C_6H_4CH_2NMe_2)}\overline{\mathrm{Pd}\{Ph_2PC[{=}C(O}\mathrm{)\text{-}Ph][(MeO_2C)C{=}C(H)(CO_2Me)]\}}$ (13). A solution of **12** (0.150 g, 0.22 mmol) in THF (10 mL) was refluxed for 24 h. The solvent was removed in vacuo. Dissolution of the residue in CH$_2$Cl$_2$ and addition of pentane afforded pale yellow crystals of **13**, which were suitable for X-ray analysis; yield 0.145 g, 97%; mp 180 °C dec. When the reaction was performed in refluxing CH$_2$Cl$_2$, the conversion was complete only after 6 days. Infrared data (KBr): 1725 sh, 1715 s, br, 1592 m, sh, 1576 ms, 1494 m, 1480 sh, 1455 s, 1425 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.80 (d, 6 H, NMe$_2$, ^4J(PH) = 2.1 Hz), 3.02 (s, 3 H, *Me*O$_2$CCH, assignment made with NOE experiment), 3.41 (s, 3 H, *Me*O$_2$CCCH), 3.89 (d, 2 H, NCH$_2$, ^4J(PH) = 1.6 Hz), 5.14 (d, 1 H, *H*CCO$_2$Me, ^4J(PH) = 1.4 Hz), 6.65–7.93 (19 H, aromatic H). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 38.2 (s). Anal. Calcd for $C_{35}H_{34}NO_5PPd$ (M = 686.05): C, 61.28; H, 5.00; N, 2.03. Found: C, 62.01; H, 5.08; N, 1.70.

Crystal Structure Determination of *u*-*trans*-4. Pale yellow parallelepipedic single crystals of *u-trans*-4 were grown by slow diffusion of pentane into a dilute CH$_2$Cl$_2$ solution of the complex. All data were collected at room temperature (23 ± 2 °C). Precise lattice parameters were determined by standard Enraf-Nonius least-squares methods using 25 carefully selected reflections. Intensity data were collected on an automatic four-circle diffractometer. No intensity decay was observed during the data collection period. For all subsequent computations the Enraf-Nonius SDP package was used.[14] Intensities were corrected for Lorentz–polarization factors. Absorption corrections were omitted in view of the low linear absorption coefficient. The crystal structure was solved by using the Patterson and Fourier difference methods and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\sum(w|F_o| - |F_c|)^2$, where the weight w is $[^1/_4((\sigma^2(I)/I + (0.05I)^2/I)]^{-1}$. Hydrogen atoms were introduced by their computed coordinates (distances C–H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of B = 5.0 Å^2. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non-hydrogen atoms were obtained from standard source.[15] Refinement results are given in Table I. Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycle (Table S-I), anisotropic thermal parameters for all non-hydrogen atoms (Table S-II), a complete list of bond distances and angles (Table S-III), a listing of angles between selected planes (Table S-IV), and a listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-V) are available as supplementary material.[16]

Crystal Structure Determination of *l*-*cis*-8. Parallelepipedic pale yellow single crystals of *l-cis*-8 were obtained by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of the complex. The data collection and the structure solution was performed as for *u-trans*-4. However, intensity data were corrected for absorption by using the empirical method of Walker and Stuart.[17] The weighting scheme was $[^1/_4((\sigma^2(I)/I + (0.05I)^2/I)]^{-1}$. Refinement results are given in Table I. Atomic coordinates (Table S-VI), anisotropic thermal parameters for all non-hydrogen atoms (Table S-VII), a complete list of bond distances and angles (Table S-VIII), a list of angles between selected planes (Table S-IX), and a listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-X) are available as supplementary material.[16] The compound crystallizes with a 0.5CH$_2$Cl$_2$ molecule. The arrangement of the solvent molecules around the C_2 axis is statistically disordered.

Acknowledgment. We thank the CNPq (Brazil) for a grant to T.M.G.C. and the C.N.R.S. for financial support and Mrs. A. Degrémont for technical assistance. We also appreciate interesting discussions with Dr. M. A. Luke.

Supplementary Material Available: Tables of atomic coordinates (Tables S-I and S-VI) and anisotropic thermal parameters (Tables S-II and S-VII), complete lists of bond distances and angles (Tables S-III and S-VIII), and listings of angles between selected planes (Tables S-IV and S-IX for *u-trans*-4 and *l-cis*-8, respectively) (32 pages); listings of observed and calculated structure factors (Tables S-V and S-X) (42 pages). Ordering information is given on any current masthead page.

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(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vol. IV, p 99.

(16) See paragraph at the end of paper regarding supplementary material.

(17) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.