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Complexes with Functional Phosphines. 13.¹ Reactivity of Coordinated Phosphino Enolates and Metallacycles toward Chlorophosphines with Diastereoselective Formation of P-O and P-C Bonds. Alkaline Hydrolysis of Coordinated Phosphinites Leading to Oxodiarylphosphoranido Ligands. Synthesis and Molecular Structure of

cis-[Pd{Ph₂PCH=C(O)Ph}{PhP(O)(CH₂C₉H₆N)}]

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Chlorodiphenylphosphine reacts with *cis*-[M{Ph₂PCH=C(O)Ph}₂] (M = Ni (1), Pd (2), Pt (3)) to afford the complexes *cis*-[MCl₂{Ph₂PCH=C(Ph)OPPh₂}] (4-6, respectively), resulting from selective coupling of the oxygen atom of the enolate with phosphorus. Phosphorus double functionalization is achieved in the reaction of dichlorophenylphosphine with [(C⁻N)Pd-Ph₂PCH=C(O)Ph] (C⁻N = *o*-C₆H₄CH₂NMe₂ (7), C₁₀H₈N (8)) in the presence of pyridine, affording *cis*-[PdCl₂{Ph₂PCH=C(Ph)OP(Ph)(*o*-C₆H₄CH₂NHMe₂)}]Cl (9) and *cis*-[PdCl₂{Ph₂PCH=C(Ph)OP(Ph)(CH₂C₉H₆NH)}]Cl (10), respectively. These constitute the first examples of coupling reactions between a phosphorus atom and a transition-metal-bound carbon atom of a cyclometalated ligand. The new P⁻P⁻N ligands are formed in a diastereoselective reaction and behave as P,P chelates to palladium. Compounds 9 and 10 are readily hydrolyzed in alkaline solutions, affording the oxodiarylphosphoranido complexes *cis*-[Pd{Ph₂PCH=C(O)Ph}{PhP(O)(*o*-C₆H₄CH₂NMe₂)}] (11) and *cis*-[Pd{Ph₂PCH=C(O)Ph}{PhP(O)(CH₂C₉H₆N)}] (12), respectively. The molecular structure of 12·CHCl₃ has been determined by X-ray diffraction: triclinic, space group P $\bar{1}$, with Z = 2, a = 10.749 (5) Å, b = 12.285 (3) Å, c = 14.022 (5) Å, α = 70.61 (2)°, β = 86.80 (3)°, γ = 81.54 (3)°, and V = 1727.8 Å³. The structure has been refined for the 2612 reflections with F_o² > 3σ(F_o²) to R = 0.057 and R_w = 0.067. The coordination of the palladium deviates from the ideal planar geometry mainly because of the lack of flexibility of the P,N chelate, which prevents the nitrogen atom from occupying a position in the coordination plane. This also leads to a somewhat elongated Pd-N bond (Pd-N = 2.207 (7) Å). All complexes were characterized by elemental analysis, IR spectroscopy, and ¹H and ³¹P{¹H} NMR spectroscopy.

Introduction

The synthesis of polydentate and/or asymmetric ligands containing mixed sets of donor atoms is a subject of considerable current interest, in particular with respect to the development of new homogeneous catalysts containing phosphorus ligands. However, the synthesis of such ligands and the complexes thereof often requires multistep manipulations with sometimes low yields and/or special reaction conditions.^{2a} Thus, for example, unsymmetrical triarylphosphines are usually obtained by stepwise treatment of an arylchlorophosphine with different organometallics such as aryllithium, Grignard, organozinc, or organocadmium reagents.³ Formation of a P-X bond (X = C, O, N, ...) by coupling of trivalent phosphorus reagents with transition-metal-coordinated ligands has been used rarely for the synthesis of coordinated phosphorus ligands.^{4,5} We have previously reported that metallacyclic compounds can provide a template matrix allowing such coupling reactions to be performed with high selectivity.⁶ In order to investigate the possibility of generalizing this reaction to complexes containing two different metallacycles, thereby generating compounds with a chiral phosphorus atom, bicyclic complexes were recently treated with PhPCl₂⁷ (see Scheme I). This synthetic strategy has considerable potential for the chemo- and stereoselective construction of polyfunctional ligands. We now wish to report full details of the one-pot synthesis of coordinated polydentate phosphine-phosphinite ligands and of new chiral functional phosphites by metal-assisted condensation of chlorophosphines with air-stable nickel, palladium, or platinum metallacyclic compounds. Some aspects of this work have been presented elsewhere.^{6,7} We also describe here the synthesis and crystal structure of the new oxodiarylphosphoranido, phosphino enolate complex *cis*-[Pd{Ph₂PCH=C(O)Ph}{PhP(O)-

CH₂C₉H₆N}] (12), obtained by alkaline hydrolysis of *cis*-[PdCl₂{Ph₂PCH=C(Ph)OP(Ph)(CH₂C₉H₆NH)}]Cl (10).

Results

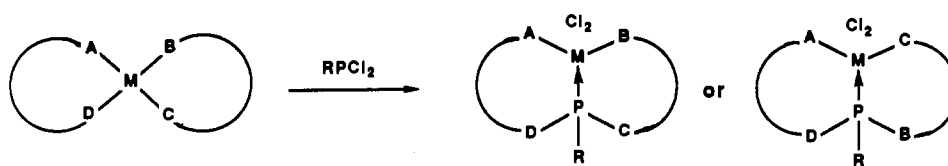
The transformations observed in this work are summarized in Schemes II and III. Preparative and analytical details for the new complexes are given in the Experimental Section. The phosphino enolate complexes 1-3 react readily at room temperature with 2 equiv of diphenylchlorophosphine, affording in good yields the complexes *cis*-[MCl₂{Ph₂PCH=C(Ph)OPPh₂}] (4-6), respectively (eq 1, Scheme II).⁸

When the complexes 7 and 8 were reacted with 2 equiv of Ph₂PCl, complex 5 was formed in high yield with respect to palladium (eq 2, Scheme II). When only 1 equiv of Ph₂PCl was used, ca. 50% of the precursor complex was recovered. The ³¹P{¹H} NMR spectra of the crude reaction mixtures of eq 2 revealed the

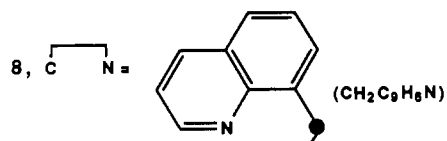
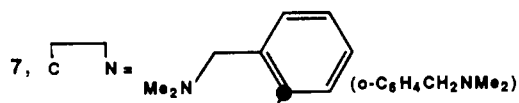
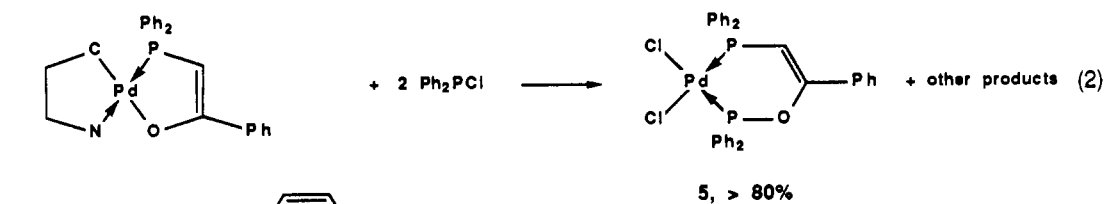
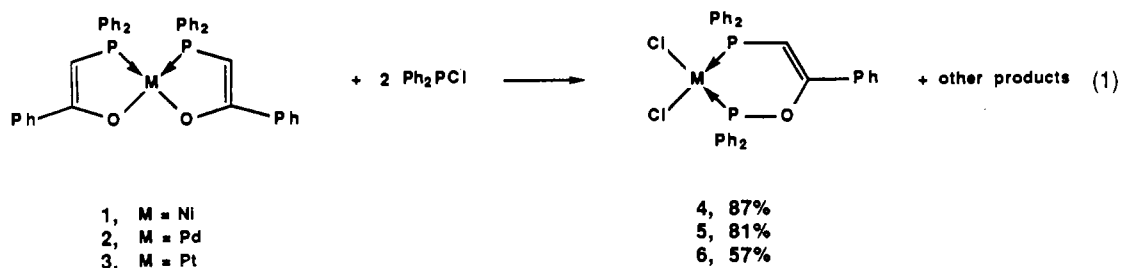
- (1) Part 12: Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279.
- (2) (a) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon: Oxford, England, 1979; Vol. 2, Chapter 10, p 1121. (b) *Ibid.*, p 1164.
- (3) Maier, L. In *Organo Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Ed.; Wiley-Interscience: New York, 1972-1974; Vol. 1.
- (4) Sokolov et al. reported the synthesis of 1-(diphenylphosphino)-2-(dimethylamino)methylferrocene using cyclometalated palladium complexes. However, isolation of the complex resulting from carbon-phosphorus bond formation failed; see: Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1980**, *202*, C58.
- (5) A reaction involving Schiff base transition-metal complexes and PCl₃ has been reported; see: Hobday, M. D.; Smith, T. D. *J. Chem. Soc. A* **1970**, 1085.
- (6) Braunstein, P.; Matt, D.; Nobel, D.; Balegroune, F.; Bouaoud, S.-E.; Grandjean, D.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1988**, 353.
- (7) Braunstein, P.; Matt, D.; Nobel, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1530.
- (8) We have previously reported that these complexes could also be obtained on refluxing a toluene solution of [MCl₂{Ph₂PCH₂C(O)Ph}]₂; see ref 6 for M = Ni, Pt and ref 9 for M = Pd.
- (9) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

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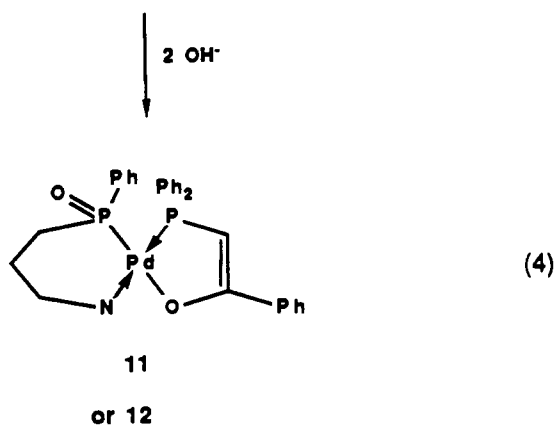
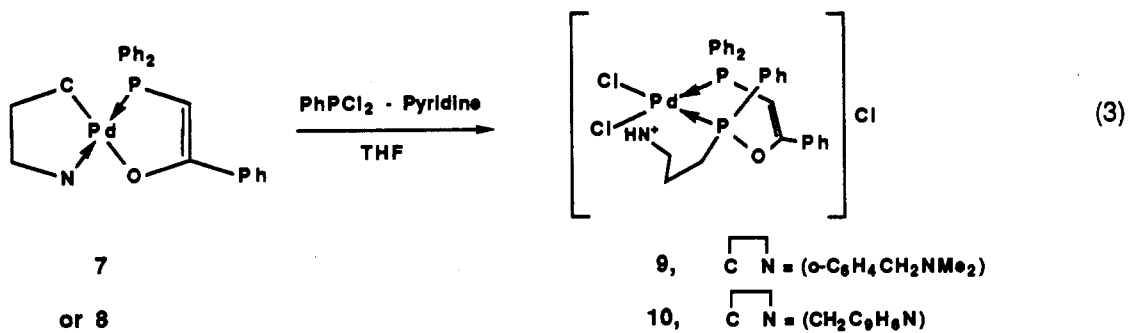
Scheme I



Scheme II



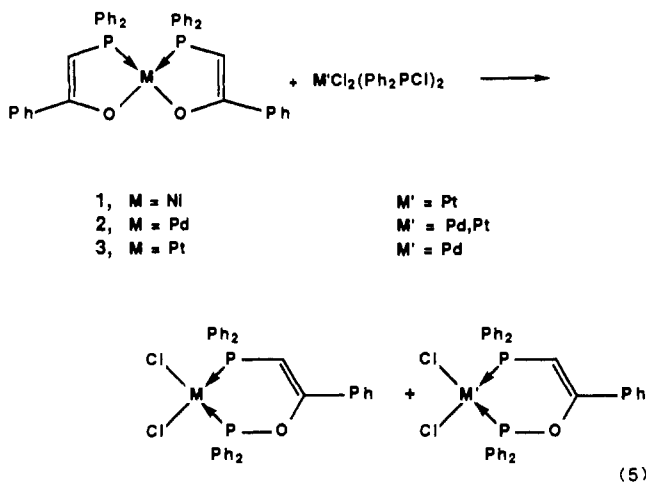
Scheme III



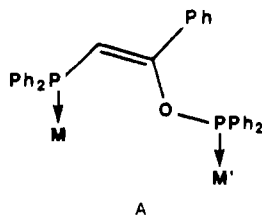
presence of other phosphorus-containing compounds, and this suggested that the cyclometalated ligand had also reacted with the chlorophosphine. To confirm this hypothesis, we reacted **7** and **8** with a mixture of commercial phenyldichlorophosphine and pyridine (eq 3, Scheme III). The products, complexes **9** and **10**, respectively, contain a new phosphine-phosphinite ligand, resulting from a double coupling reaction between the "PhP" moiety and the metalated carbon and oxygen atoms of the precursor complexes. When they stand in wet CH_2Cl_2 solutions, **9** and **10** slowly transform. By addition of bases such as NEt_3 and Na_2CO_3 to such solutions, this reaction becomes instantaneous and leads to the oxodiarylphosphoranido complexes **11** and **12**, respectively (eq 4, Scheme III).

Discussion

Reactions of Chlorophosphines with *cis*-[M{Ph₂PCH=C(O)Ph}₂]. Interestingly, in the reaction shown in eq 1, Scheme II, the enolate moieties undergo coupling with the incoming phosphorus via their oxygen atom and not via the carbon atom α to phosphorus. This contrasts with the previously reported reactions of complexes **1**–**3** with aryl isocyanates in which a C–C coupling reaction occurred.^{1,10} In the reaction of eq 1, the formation of an intermediate containing the P–C coupling product $\text{Ph}_2\text{PCH}(\text{C}(\text{O})\text{Ph})\text{PPh}_2$ appears unlikely since its subsequent transformation into the phosphine-phosphinite ligand, which implies cleavage of a P–C bond, has been reported to require more severe conditions, at least in the coordination sphere of tungsten.¹¹ Equilibration of the reaction of eq 1 would suggest formation of 1 equiv of the free ligand $\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2$. However, it was not trapped, e.g., in the form of **5** upon addition of $\text{PdCl}_2(\text{PhCN})_2$ to the reaction mixture. We have now found that metal-coordinated diphenylchlorophosphine also reacted with the enolato complexes **1**–**3** (1:1 mole ratio, THF, 25–50 °C, 3 h) to give a mixture containing mainly the mononuclear complexes shown in eq 5.



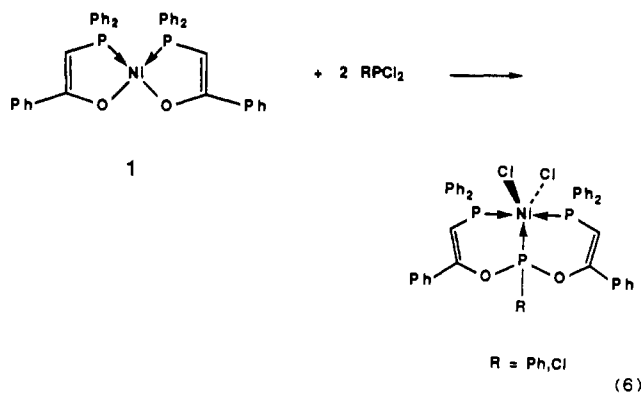
Although there was no evidence for the formation of the initially hoped for units of type A, such intermediate steps cannot be ruled



- (10) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. J. *Chem. Soc., Chem. Commun.* **1987**, 488.
(11) Coordinated $\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2$ has been generated by the light-induced conversion of $[\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}(\text{C}(\text{O})\text{Ph})\text{PPh}_2)]$ into $[\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2)]$ via P–C bond cleavage and P–O bond formation; see: Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863.

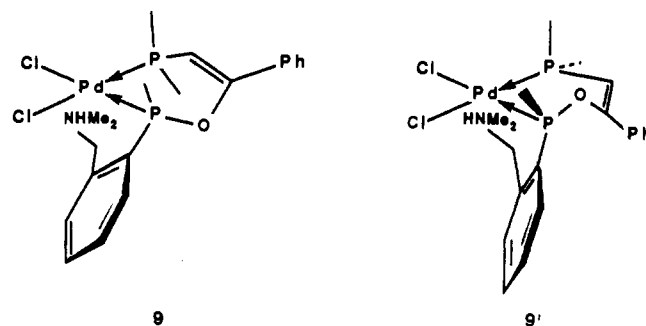
out. Note that it has been recently shown that the buildup of heterobinuclear complexes with the bridging diphosphine $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, a ligand of size comparable to that of $\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2$, may be achieved from mononuclear complexes.¹² The preference for chelation exhibited by this phosphine-phosphinite ligand is obviously the result of geometric factors due to the presence of the heteroatom and the double bond.¹³

Phosphorus Double-Functionalization Reactions. In order to illustrate the scope of the synthetic strategy shown in Scheme I, the reaction depicted in eq 1 has been extended to the synthesis of tridentate ligands. Thus, as reported earlier,⁶ reacting $\text{Ph}_x\text{PCL}_{3-x}$ ($x = 0, 1$) with **1** leads to coupling of the phosphorus atom with both nickel-coordinated enolates (eq 6). An answer to the question



whether this high-yield metal-controlled ligand synthesis could also be applied to the "one pot" buildup of heterodifunctional phosphine ligands was provided by reacting PhPCL_2 with palladium complexes containing two *different* metallacycles (eq 3, Scheme III). Indeed, a coupling of the incoming "PPh" moiety with both chelates occurs, thus generating a chiral phosphorus atom. The geometry of **9** was confirmed by an X-ray diffraction analysis.⁷ Pyridine was used in this reaction in order to trap, as pyridinium chloride, the HCl always present in commercial PhPCL_2 and thus prevent protonolysis of the coordinated phosphino enolate. During the course of the reaction, the pyridinium cation releases its proton to form the hydrochlorides **9** and **10**, which, in this form, could be better isolated and purified. To our knowledge, this is the first example of coupling reactions between a phosphorus atom and a transition-metal-bound carbon atom of a cyclometalated ligand.⁴

The cations of **9** and **10** contain a chiral phosphorus atom and a nonplanar chelate ring, for which two conformations are conceivable (**9** and **9'**). The CPK molecular model of **9** shows that,



because of steric crowding, ring inversion, i.e. the transformation $\mathbf{9} \rightarrow \mathbf{9}'$, is a difficult process. The model also shows that the stereochemistry depicted for **9** minimizes the steric repulsions within the molecule.⁷ The reactions displayed in eq 3 are diastereoselective, complexes **9** and **10** being formed in ca. 70% yield, as shown by ³¹P NMR. The other products, possibly

- (12) (a) Keiter, R. L.; Kaiser, S. L.; Hansen, N. P.; Brodack, J. W.; Cary, L. W. *Inorg. Chem.* **1981**, *20*, 283. (b) Iggo, J. A.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1009.
(13) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. J. *Chem. Soc., Dalton Trans.* **1979**, 1972.

Table I. Selected Interatomic Distances (Å) and Angles (deg) in *cis*-[Pd(Ph₂PCH=C(O)Ph){PhP(O)CH₂C₈H₆N}]·CHCl₃ (**12**·CHCl₃)

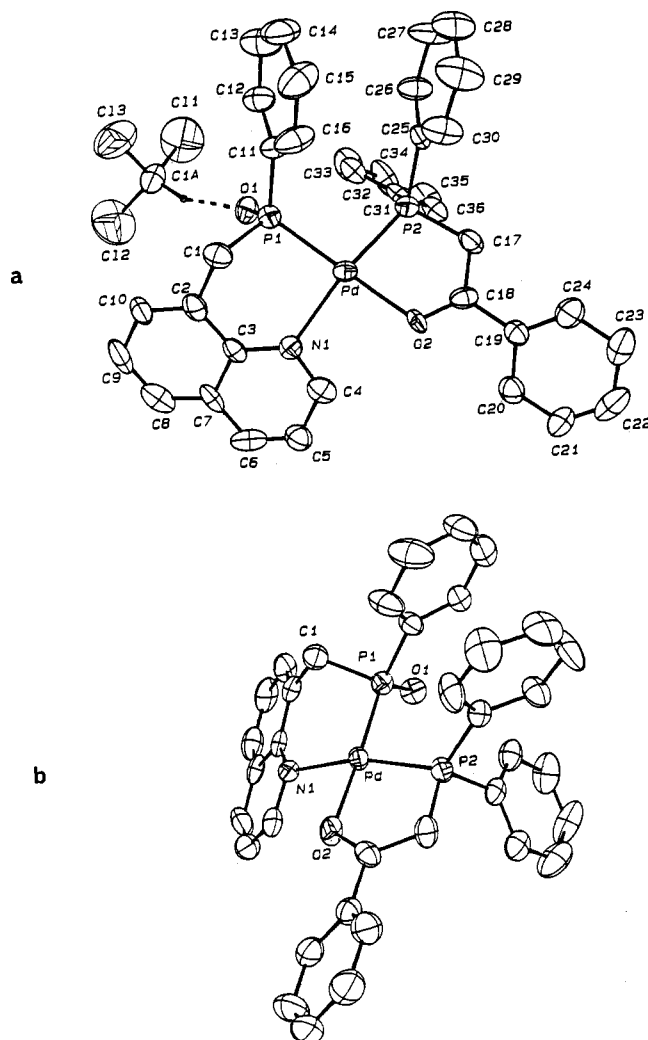
Bond Distances			
Pd-P(1)	2.210 (3)	O(1)-H(1A)	1.885 (5)
Pd-P(2)	2.234 (2)	O(2)-C(18)	1.258 (10)
Pd-O(2)	2.093 (6)	C(1A)-H(1A)	1.082 (9)
Pd-N(1)	2.207 (7)	C(17)-C(18)	1.408 (11)
P(1)-O(1)	1.478 (6)	C(18)-C(19)	1.486 (11)
P(1)-C(11)	1.820 (9)	C(18)-O(2)	1.258 (10)
P(1)-C(1)	1.816 (9)	N(1)-C(3)	1.338 (10)
P(2)-C(17)	1.768 (9)	C(3)-C(2)	1.438 (12)
P(2)-C(25)	1.815 (8)		
P(2)-C(31)	1.824 (9)		
Bond Angles			
O(2)-Pd-P(2)	83.2 (2)	Pd-N(1)-C(3)	127.7 (6)
O(2)-Pd-N(1)	90.6 (2)	N(1)-C(3)-C(2)	124.2 (8)
N(1)-Pd-P(1)	90.4 (2)	C(3)-C(2)-C(1)	116.4 (8)
P(1)-Pd-P(2)	97.18 (9)	P(1)-C(1)-C(2)	111.0 (6)
Pd-P(2)-C(17)	101.7 (3)	Pd-P(1)-C(1)	100.2 (3)
Pd-O(2)-C(18)	117.3 (5)	Pd-P(1)-O(1)	117.9 (3)
C(17)-C(18)-O(2)	125.5 (9)	C(1)-P(1)-C(11)	100.4 (4)
P(2)-C(17)-C(18)	112.3 (7)		

containing the other diastereomer of **9** and **10**, respectively, have not been identified. The first step of the reaction is likely to be the coordination of PhPCl₂ to the metal, but the detailed sequence of the following events leading to the products is not known at the moment.

Hydrolysis of the Coordinated Phosphine-Phosphinite Ligand into an Oxodiarylphosphoranido Ligand. This reaction is depicted in Scheme III. Cleavage of the P-O bond, which regenerates the enolate ligand [Ph₂PCH=C(O)Ph]⁻, results from nucleophilic attack of OH⁻ on phosphorus. Deprotonation by the base of the ammonium and of the intermediately formed P-OH group leads to the chelating oxophenylarylophosphoranido-amine ligand present in **11** and **12**. Typical features in the infrared spectra of **11** and **12** include a strong absorption at ca. 1510 cm⁻¹, characteristic of the presence of the chelating phosphino enolate [Ph₂PCH=C(O)Ph]⁻.^{6,9} In their ³¹P{¹H} NMR spectra, two singlets are observed and the absence of P-P coupling is consistent with a *cis* coordination of these atoms, as noted in complexes **9** and **10**. The resonance of the PCH proton of the [Ph₂PCH=C(O)Ph]⁻ enolate moiety of **11** and **12** is shifted to higher field when compared to that in **9** or **10** but still appears as a doublet of doublets, owing to coupling with both phosphorus atoms. The occurrence of an ABXY pattern for the CH₂N protons and the presence of two *N*-methyl signals in the ¹H NMR spectrum of **11** are consistent with the presence of a chiral phosphorus atom.

It is interesting to note that Shaw et al. reported a reaction related to that of eq 4 in which the complex [W(CO)₄(Ph₂POH)(Ph₂PCH₂C(O)Ph)] was formed upon irradiation of [W(CO)₄{Ph₂PCH=C(Ph)OPPh₂}] in the presence of traces of water.¹¹ Complete hydrolysis of the ligand had occurred, whereas in our case, the presence of base allows both the conversion of the intermediately formed P-OH into the P=O bond as well as the recovery of the chelating [Ph₂PCH=C(O)Ph]⁻ anion. The reaction mechanism is not known in detail, but we believe that it is related to the well-studied alkaline hydrolysis of phosphonium salts.^{2b}

The structure of **12** was confirmed by an X-ray diffraction study. An ORTEP view of the structure of **12**·CHCl₃ is depicted in Figure 1, selected interatomic distances and angles are given in Table I, and crystal data are displayed in Tables II and S-I (supplementary material). Selected least-squares planes are presented in Table S-V (supplementary material).¹⁴ The palladium atom has a somewhat distorted square-planar environment (maximum deviation out of the mean plane is -0.215 Å for N(1) and P(2)) due to the difficulty of the sp² nitrogen atom in occupying the fourth coordination site without imposing a large strain

**Figure 1.** (a) ORTEP drawing of *cis*-[Pd(Ph₂PCH=C(O)Ph){PhP(O)CH₂C₈H₆N}]·CHCl₃ (**12**·CHCl₃). (b) View showing the puckering of the P(1),N(1) chelate.**Table II.** Crystal Data and Data Collection for *cis*-[Pd(Ph₂PCH=C(O)Ph){PhP(O)CH₂C₈H₆N}]·CHCl₃ (**12**·CHCl₃)

formula:	C ₃₆ H ₂₉ NO ₂ P ₂ Pd·CHCl ₃	formula wt:	795.36
<i>a</i>	10.749 (5) Å	space group:	P $\bar{1}$ (No. 2)
<i>b</i>	12.285 (3) Å	<i>T</i>	23 ± 2 °C
<i>c</i>	14.022 (5) Å	λ	0.710730 Å
α	70.61 (2)°	ρ_{calc}	1.529 g/cm ³
β	86.80 (3)°	μ	8.88 cm ⁻¹
γ	81.54 (3)°	<i>R</i> (<i>F</i> _o)	0.057
<i>V</i>	1727.8 Å ³	<i>R</i> _w (<i>F</i> _o)	0.057
<i>Z</i>	2		

to the chelate [PhP(O)N]⁻ to which it belongs. The latter effect is also measured by the rather long Pd-N(1) distance of 2.207 (7) Å but, however, does not imply a curvature of the plane constituted by the two fused aromatic rings of the P,N ligand as found in some palladium complexes with ((8-methyl-2-quinolyl)methyl)di-*tert*-butylphosphine-*N*,*P*.¹⁵ The six-membered chelate ring is not planar, and the angle between the plane C(1)C(2)C(3)N(1) (which contains the 8-methylquinoline) and the plane N(1)Pd(1) is 28.7°. Dimensions within the 8-methylquinoline moiety are normal.¹⁶ That electron delocalization occurs within the phosphino enolate chelate is shown by the values of the C(17)-C(18) (1.408 (11) Å) and C(18)-O(2) (1.258 (10)

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

(15) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1974.(16) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410.

Å) distances. These values compare with those found in the other structurally characterized complexes containing this three-electron-donor ligand, namely $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph})]^{17}$ and *cis*- $[\text{Ni}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]^{18}$. The complex crystallized with one molecule of CHCl_3 . The short O(1)–H(1A) distance (1.885 (5) Å) indicates hydrogen bonding between the solvent molecule and O(1).

In conclusion, we have shown that chlorophosphines readily react with M(II) complexes (M = Ni, Pd, Pt) containing three-electron-donor $[\text{R}_2\text{P}^-\text{O}]^-$ and/or $[\text{R}_2\text{N}^-\text{C}]^-$ chelates to afford P–O and P–C coupling products. When performed with dichlorophosphines, this reaction allows the preparation of chiral phosphorus compounds from air-stable organometallics, and we are presently investigating the potential of this reaction. Furthermore, hydrolysis of the P–O bond of the coordinated phosphinite has led to the preparation and characterization of palladium complexes containing oxodiarylphosphoranido anions. Related ligands, also called diarylphosphidoxo, have been used recently as bridging groups in polynuclear complexes.¹⁹

Experimental Section

All reactions were performed in Schlenk-type flasks under argon. Details of the experimental procedure used throughout this work, including reagents and solvents, have been described in previous papers.^{1,6} The ¹H and ³¹P{¹H} NMR spectra were recorded at 200 and 81 MHz, respectively, on a FT Bruker WP-200 SY instrument. Commercial PhPCl_2 and Ph_2PCL were saturated with argon prior to use. The complexes *cis*- $[\text{M}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]$, M = Ni (1), Pd (2), Pt (3),⁶ and $[(\text{C}_6\text{H}_5)_2\text{N}\{\text{Pd}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}\}_2\text{C}=\text{N}-\alpha\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2]$ (7),⁹ $\text{C}_{10}\text{H}_8\text{N}$ (8),⁹ were prepared according to the reported methods.

cis- $[\text{NiCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2\}]$ (4). A solution of Ph_2PCL (0.100 g, 0.45 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of *cis*- $[\text{Ni}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]$ (0.140 g, 0.21 mmol) in CH_2Cl_2 (10 mL). After it was stirred for 0.25 h, the solution was filtered and the solvent removed in vacuo. The orange precipitate was washed with pentane and recrystallized from CH_2Cl_2 /pentane (yield 0.112 g, 87%; mp >230 °C). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{NiOP}_2$ ($M_r = 618.13$): C, 62.18; H, 4.24. Found: C, 61.96; H, 4.16. IR (KBr): 1602 s, 1569 m, 1477 m cm^{-1} . ¹H NMR (CDCl_3): δ 5.72 (d, 1 H, PCH, $J(\text{PH}) = 2.5$ Hz), 7.23–8.00 (25 H, aromatic H). ³¹P{¹H} NMR (CDCl_3): δ 2.0 (d, 1 P, PCH, $J(\text{PP}) = 106$ Hz), 126.6 (d, 1 P, PO, $J(\text{PP}) = 106$ Hz).⁸

cis- $[\text{PdCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2\}]$ (5). A solution of Ph_2PCL (0.452 g, 2.05 mmol) in THF (10 mL) was added to a stirred solution of *cis*- $[\text{Pd}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]$ (0.713 g, 1.00 mmol) in THF (10 mL). After the mixture was stirred for 2 h, the solvent was removed in vacuo and the solid was washed with cold ether. Recrystallization from CH_2Cl_2 /pentane afforded white crystals of 5 (yield 0.539 g, 81%; mp >230 °C, slow dec). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{OP}_2\text{Pd}$ ($M_r = 665.81$): C, 57.73; H, 3.94. Found: C, 57.71; H, 3.96. IR, ¹H NMR, ³¹P{¹H} NMR, and MS data are in agreement with the values published for this complex obtained by thermal treatment of $[\text{PdCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]^{8,9}$ or by the reaction of 7 or 8 with 2 equiv of Ph_2PCL in THF (yield >80%).¹⁰

cis- $[\text{PtCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OPPh}_2\}]$ (6). A solution of Ph_2PCL (0.150 g, 0.68 mmol) in THF (5 mL) was added to a stirred solution of *cis*- $[\text{Pt}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}_2]$ (0.250 g, 0.31 mmol) in THF (10 mL). After the mixture was stirred for 1 h, the solvent was removed in vacuo and the resulting white solid was washed with ether. Recrystallization from CH_2Cl_2 /pentane afforded white crystals of 6 (yield 0.134 g, 57%; mp >260 °C). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{OP}_2\text{Pt}$ ($M_r = 754.51$): C, 50.94; H, 3.47. Found: C, 51.01; H, 3.33. IR (KBr): 1598 s, 1570 m cm^{-1} . ¹H NMR (CD_2Cl_2): δ 6.02 (dd with Pt satellites, 1 H, PCH, $J(\text{PH}) = 2.6$ and 3.7 Hz, $^3J(\text{PtH}) = 66$ Hz), 7.15–8.18 (25 H, aromatic H). ³¹P{¹H} NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$): δ -14.5 (d with Pt satellites, 1 P, PCH, $J(\text{PP}) = 24$ Hz, $^1J(\text{PtP}) = 3368$ Hz), 99.8 (d, with Pt satellites, 1 P, PO, $J(\text{PP}) = 24$ Hz, $^1J(\text{PtP}) = 4040$ Hz).⁸

Table III. Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B, Å ²
Pd	0.16292 (9)	0.12965 (8)	0.44528 (7)	3.22 (2)
Cl(1)	0.4708 (6)	0.3605 (4)	0.0084 (5)	13.9 (2)
Cl(2)	0.5958 (5)	0.1307 (6)	0.0548 (5)	14.3 (2)
Cl(3)	0.3536 (5)	0.1852 (5)	-0.0272 (4)	11.9 (2)
P(1)	0.1888 (3)	0.1490 (2)	0.2833 (2)	3.58 (7)
P(2)	0.0797 (3)	0.3136 (2)	0.4248 (2)	3.49 (7)
O(1)	0.3022 (7)	0.1967 (6)	0.2315 (5)	4.5 (2)
O(2)	0.1234 (7)	0.1066 (5)	0.5980 (5)	4.1 (2)
N(1)	0.2892 (8)	-0.0374 (7)	0.4866 (6)	3.4 (2)
C(1)	0.194 (1)	-0.0014 (9)	0.2891 (9)	4.5 (3)
C(1A)	0.458 (1)	0.215 (1)	0.0502 (9)	5.8 (4)
C(2)	0.322 (1)	-0.0706 (8)	0.3232 (9)	4.2 (3)
C(3)	0.358 (1)	-0.0854 (8)	0.4245 (8)	3.4 (3)
C(4)	0.328 (1)	-0.0616 (9)	0.5796 (9)	4.5 (3)
C(5)	0.444 (1)	-0.136 (1)	0.6164 (9)	4.8 (3)
C(6)	0.514 (1)	-0.178 (1)	0.560 (1)	6.0 (4)
C(7)	0.479 (1)	-0.1584 (8)	0.4589 (9)	4.1 (3)
C(8)	0.553 (1)	-0.198 (1)	0.393 (1)	6.2 (4)
C(9)	0.519 (1)	-0.177 (1)	0.293 (1)	6.6 (4)
C(10)	0.398 (1)	-0.1135 (9)	0.2636 (9)	5.2 (3)
C(11)	0.050 (1)	0.2160 (9)	0.2059 (8)	4.1 (3)
C(12)	0.062 (1)	0.305 (1)	0.1158 (9)	5.1 (3)
C(13)	-0.041 (1)	0.355 (1)	0.056 (1)	7.2 (4)
C(14)	-0.154 (1)	0.320 (1)	0.087 (1)	7.5 (4)
C(15)	-0.169 (1)	0.234 (1)	0.177 (1)	7.7 (5)
C(16)	-0.067 (1)	0.182 (1)	0.2365 (9)	6.3 (4)
C(17)	0.037 (1)	0.3059 (9)	0.5502 (9)	4.4 (3)
C(18)	0.072 (1)	0.1942 (9)	0.6200 (8)	3.8 (3)
C(19)	0.044 (1)	0.1805 (9)	0.7280 (8)	4.0 (3)
C(20)	0.129 (1)	0.1037 (9)	0.8009 (9)	4.7 (3)
C(21)	0.103 (1)	0.092 (1)	0.9005 (9)	6.3 (4)
C(22)	0.006 (1)	0.147 (1)	0.9324 (9)	7.0 (4)
C(23)	-0.085 (1)	0.222 (1)	0.8621 (9)	6.4 (4)
C(24)	-0.058 (1)	0.235 (1)	0.7613 (9)	5.2 (3)
C(25)	-0.059 (1)	0.3901 (8)	0.3507 (8)	3.3 (3)
C(26)	-0.059 (1)	0.493 (1)	0.2727 (9)	5.1 (3)
C(27)	-0.172 (1)	0.552 (1)	0.226 (1)	7.7 (5)
C(28)	-0.280 (1)	0.508 (1)	0.258 (1)	7.2 (4)
C(29)	-0.283 (1)	0.408 (1)	0.333 (1)	7.8 (5)
C(30)	-0.174 (1)	0.348 (1)	0.380 (1)	5.9 (4)
C(31)	0.198 (1)	0.4126 (8)	0.3823 (8)	3.6 (3)
C(32)	0.252 (1)	0.4306 (9)	0.2876 (9)	4.9 (3)
C(33)	0.346 (1)	0.504 (1)	0.258 (1)	7.3 (4)
C(34)	0.379 (1)	0.558 (1)	0.320 (1)	7.8 (4)
C(35)	0.328 (1)	0.541 (1)	0.413 (1)	7.9 (4)
C(36)	0.236 (1)	0.467 (1)	0.4459 (9)	4.9 (3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters: B (Å²) = $1/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab(\cos \gamma) + \beta_{13}ac(\cos \beta) + \beta_{23}bc(\cos \alpha)]$.

cis- $[\text{PdCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OP}(\text{Ph})(\alpha\text{-C}_6\text{H}_4\text{CH}_2\text{NHMe}_2)\}\text{Cl}]$ (9). A solution of commercial PhPCl_2 (0.036 g, 0.20 mmol) and pyridine (0.2 mL) in THF (1 mL) was added to a stirred solution of 7 (0.100 g, 0.18 mmol) in THF (20 mL). The reaction mixture was stirred overnight. Upon concentration of the solution, a white powder precipitated. It was collected, washed with ether, and recrystallized from CH_2Cl_2 /toluene/pentane (yield 0.106 g, 68%; mp 230–245 °C dec). Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{Cl}_3\text{NOP}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$ ($M_r = 844.31$): C, 51.21; H, 4.30. Found: C, 51.20; H, 4.27. IR (KBr): 1597 s, 1567 m, 1466 s cm^{-1} . ¹H NMR (CDCl_3): δ 2.50 (d, 3 H, CH_3 , $^3J = 3.9$ Hz), 2.78 (d, 3 H, CH_3 , $^3J = 4.3$ Hz), 4.70 (δ_A) and 5.22 (δ_B) (ABMX spin system (with M = NH, X = P), 2 H, NCH_2 , $^2J(\text{AB}) = 14$ Hz, $^3J(\text{AM}) = 2.3$, and $^3J(\text{BM}) = 2.9$ Hz, $^4J(\text{AX}) \approx 0$ Hz, $^4J(\text{BX}) = 8.5$ Hz), 5.90 (dd, 1 H, PCH, $J(\text{PH}) = 1.3$, 6.6 Hz), 6.94–8.65 (24 H, aromatic H), 12.41 (broad s, 1 H, NH). ³¹P{¹H} NMR (CDCl_3): δ 2.0 (s, PhPO), 126.2 (s, PhPO).

cis- $[\text{PdCl}_2\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{OP}(\text{Ph})(\text{CH}_2\text{C}_6\text{H}_5\text{NH})\}\text{Cl}]$ (10). A solution of commercial PhPCl_2 (0.108 g, 0.60 mmol) and pyridine (0.4 mL) in ether (2 mL) was added to a stirred suspension of 8 (0.315 g, 0.57 mmol) in ether (30 mL). The reaction mixture was stirred overnight, and a pale yellow precipitate was formed. The latter was collected, washed with ether, and recrystallized from CH_2Cl_2 /hexane (yield 0.293 g, 67%; mp 230 °C dec). Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{NOP}_2\text{Pd}$ ($M_r = 767.35$): C, 56.35; H, 3.94; N, 1.83. Found: C, 55.70; H, 4.05; N, 1.96. IR (KBr): 1601 s, 1570 m, 1495 m, 1475 w cm^{-1} . ¹H NMR (CDCl_3): δ 5.18 (δ_A) and 5.37 (δ_B) (ABX spin system (with X = P(O)), 2 H,

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PCH_2 , ${}^2J(\text{AB}) = 13.8$ Hz, ${}^2J(\text{AX}) = 4.7$ Hz, ${}^2J(\text{BX}) = 14$ Hz), 5.51 (dd, 1 H, PCH, $J(\text{PH}) = 1.1, 7.3$ Hz), 7.18–8.78 (aromatic H), NH resonance not assigned. ${}^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): δ 4.2 (s, Ph_2PC), 135.2 (s, PO). ${}^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2): δ 34.53 (d, PCH_2 , $J(\text{PC}) = 31.6$ Hz), 91.30 (d, PCH, $J(\text{PC}) = 64.5$ Hz), 163.71 (s, CO).

cis-[Pd(Ph₂PCH=C(O)Ph)(PhP(O)(o-C₆H₄CH₂NMe₂))] (11). A 10-fold excess of Na_2CO_3 was added to a solution of **9** (0.210 g, 0.25 mmol) in undried CH_2Cl_2 (40 mL), and the reaction mixture was stirred for 8 h. The suspended Na_2CO_3 was filtered off, and the solution was concentrated under reduced pressure. Addition of pentane afforded yellow crystals of **11** (yield 0.145 g, 87%; mp 205 °C dec). Anal. Calcd for $\text{C}_{35}\text{H}_{33}\text{NO}_2\text{P}_2\text{Pd}$ ($M_r = 668.0$): C, 62.93; H, 4.98. Found: C, 62.30; H, 4.95. IR (KBr): 1581 w, 1509 s, 1480 s cm^{-1} . ${}^1\text{H}$ NMR (C_6D_6): δ 2.04 (δ_A) and 2.98 (δ_B) (ABXY spin system (with X, Y = P), 2 H, NCH_2 , ${}^2J(\text{AB}) = 12.3$ Hz, ${}^4J(\text{AX}) \approx 0$ Hz, ${}^4J(\text{BX}) = 4.1$ Hz, ${}^4J(\text{BY}) = 7.2$ Hz), 2.20 (d, 3 H, CH_3 , ${}^4J(\text{PH}) < 0.5$ Hz), 2.43 (d, 3 H, CH_3 , ${}^4J(\text{PH}) < 0.5$ Hz), 4.90 (dd, 1 H, PCH, $J(\text{PH}) = 3.0, 2.0$ Hz), 6.52–9.23 (24 H, aromatic H). ${}^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): δ 32.3 (s, Ph_2PC), 61.1 (s, PO).

cis-[Pd(Ph₂PCH=C(O)Ph)(PhP(O)CH₂C₆H₅N)] (12). This complex was prepared by starting from **10** (0.192 g, 0.25 mmol), with use of the procedure described for **11**. Addition of pentane afforded yellow crystals of **12** (yield 0.157 g, 79%; mp 180 °C dec). Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a CHCl_3 solution of **12**. Anal. Calcd for $\text{C}_{36}\text{H}_{29}\text{NO}_2\text{P}_2\text{Pd}\cdot\text{CHCl}_3$ ($M_r = 795.4$): C, 55.88; H, 3.80. Found: C, 54.53; H, 3.90. IR (KBr): 1581 w, 1513 s, 1480 s cm^{-1} . ${}^1\text{H}$ NMR (CD_2Cl_2): δ 3.49 (δ_A) and 4.16 (δ_B) (ABX spin system (with X = P(O)), 2 H, PCH_2 , ${}^2J(\text{AB}) = {}^2J(\text{AX}) = {}^2J(\text{BX}) = 14.7$ Hz), 4.84 (dd, 1 H, PCH, $J(\text{PH}) = 3.7, 1.7$ Hz), 6.82–10.39 (26 H, aromatic H). ${}^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): δ 30.0 (s, Ph_2PC), 70.2 (s, PO).

Crystal Structure Determination of 12. Crystals of **12**· CHCl_3 have a parallelepipedic habit and were obtained by slow cooling of a concentrated CHCl_3 solution of **12**. Pertinent crystal data are presented in Table II. 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.²⁰ 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 Patterson and Fourier methods²¹ 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 is $4I/[\sigma^2(I) + (0.04I)^2]$. Hydrogen atoms were introduced by their computed coordinates (C–H distance 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of $B = 5.0$ Å² except for H(1A), which was positioned by Fourier difference but not refined. The final difference map showed no significant residual peaks. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non-hydrogen atoms were obtained from standard sources.²² Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table III. Refinement results are given in Tables I and S-I (supplementary material). Hydrogen atom coordinates (Table S-II), anisotropic thermal parameters for all non-hydrogen atoms (Table S-III), all bond distances and angles (Table S-IV), and the observed and calculated structure factor amplitudes used in the refinement (Tables S-VI) are available as supplementary material.¹⁴

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Supplementary Material Available: Crystallographic data (Table S-I), hydrogen atom coordinates (Table S-II), anisotropic thermal parameters (Table S-III), all bond distances and angles (Table S-IV), and selected least-squares planes (Table S-V) (11 pages); observed and calculated structure factors (Table S-VI) (14 pages). Ordering information is given on any current masthead page.

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Solvent Effects on the Lowest Energy Excited States of Binuclear $(\text{OC})_5\text{W-L-W}(\text{CO})_5$ Complexes

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Electronic absorption, emission, photochemical, and redox potential data have been obtained for mononuclear $(\text{OC})_5\text{WL}$ and binuclear $(\text{OC})_5\text{W-L-W}(\text{CO})_5$ complexes, where L = pyrazine (pyz), 4,4'-bipyridine (bpy), and 1,2-bis(4-pyridyl)ethane (bpa), in various solvents. Low-lying ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ ligand-field (LF) and $\text{W}(\text{d}\pi) \rightarrow \pi^*(\text{L})$ charge-transfer (MLCT) transitions are observed for each complex; the MLCT absorption bands exhibit a strong negative solvatochromism. In very nonpolar solvents the MLCT band envelope indicates the presence of two components, assigned to orbitally allowed y- and z-polarized MLCT transitions. The energy positions of the MLCT transitions depend substantially on the nature of L; when L = bpa, the LF states are at lowest energy, but when L = pyz and bpy, the MLCT states are lowest lying. Changes in metal–ligand bond polarity between the ground and excited states and specific solvent–solute and induced dipolar interactions contribute to the MLCT solvatochromism; these effects are correlated with the electronic characteristics of L and the nature of the MLCT transition. Emission has been recorded from the pyz and bpy complexes at 283 K, in accordance with the MLCT assignment. Dual MLCT emission bands have been observed, but lifetime data reveal that these MLCT states are thermally equilibrated. Emission spectra exhibit solvent shifts in the direction opposite to that for absorption spectra, and this effect is rationalized on the basis of a scheme that depicts a contraction of the W–N bond in the excited state relative to the ground-state geometry. Solvent predominantly affects the nonradiative decay rates; in some cases k_{nr} data illustrate an energy gap law dependence, but specific solute–solvent and induced dipolar interactions are also deemed important. Solvent effects on redox potential data substantiate the HOMO/LUMO assignments and further indicate the extent of Franck–Condon perturbation. On photolysis the complexes undergo W–N bond dissociation; effects of solvent on this reaction efficiency are small and are incorporated in the excited-state model.

Introduction

Currently, there is substantial interest in metal complexes that are bridged through ligands containing a delocalized π system.

In particular, such ligand-bridged dimer complexes have been studied as models for inner-sphere electron-transfer processes between metal centers,¹ and they have received attention because