# Experimental and Theoretical Studies on the Reactivity of $\alpha$-Phosphino Enolates. Crystal Structures of $[K(18\text{-crown-6})][Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]$ and $[K(\text{Kryptofix-2,2,2})][Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]$[1]

Patrick Veya,[†] Carlo Floriani,*[,†] Angiola Chiesi-Villa,[‡] Carlo Guastini,[‡]
Alain Dedieu,*[,§] Florent Ingold,[§,∥] and Pierre Braunstein*[,∥]

*Section de Chimie, Université de Lausanne, CH-1005 Lausanne, Switzerland, Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy, and Laboratoire de Chimie Quantique, UPR 139 CNRS, and Laboratoire de Chimie de Coordination, URA 416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France*

*Received April 1, 1993*[⊗]

Since the potassium salts of the enolates $[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]^-$ and $[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)OEt]^-$ were found to be much less reactive toward electrophiles (e.g. $CO_2$, activated alkynes) than the corresponding palladium(II) complexes, e.g. $[(\overline{C\ N})Pd\{Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)OEt\}]$ ($\overline{CH\ N}$ = dimethylbenzylamine), we decided to isolate and structurally characterize the complexes $[K(18\text{-crown-6})][Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]$ (**4**), $[K(\text{Kryptofix-2,2,2})][Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]$ (**5**) and $[K(18\text{-crown-6})][Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)OEt]$ (**6**). Complex **4** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 13.025(1)$ Å, $b = 10.027(1)$ Å, $c = 13.976(1)$ Å, $\alpha = 106.48(1)°$, $\beta = 106.83(1)°$, and $\gamma = 97.98(1)°$. The structure was solved and refined using 4584 observed reflections measured on a Siemens AED diffractometer to a final $R$ value of 0.073. Crystals of **5** are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 14.658(1)$ Å, $b = 13.191(1)$ Å, $c = 13.3421)$ Å, $\alpha = 115.89(1)°$, $\beta = 110.33(1)°$, and $\gamma = 65.25(1)°$. For 3236 observed reflections $R$ was 0.061. In the structure of complex **4** there are discrete molecules where the oxygen atom from the phosphino enolato ligand interacts with the potassium ion at a distance of 2.630(3) Å. The structure of complex **5** consists of complexed cations and anions linked by a weak C17⋯O7 interaction which could be interpretable as a hydrogen bond. The geometry of the cryptated $K^+$ ions is normal with K⋯O distances in the range 2.770(4)–2.899(4) Å. The geometry of the anion is close to that observed in complex **4**, the main difference being due to the significant lengthening of the C37–C38 bond distance [1.404(9) Å]. The lengthening along with a more consistent planarity of the O7–C38–C37–P system indicates a more pronounced $\pi$ delocalization for the free ligand. *Ab initio* SCF calculations on the free phosphine enolate anion and on the $Li^+$ and $Na^+$ complexed phosphine enolates were also carried out in order to rationalize their reactivity as a function of their electronic properties. The palladium(II) phosphino enolate complex $[(8\text{-mq})\overline{Pd\{Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O}Ph\}]$ was reacted in THF with $AuCl(PPh_3)$ in the presence of $AgBF_4$, affording $[(8\text{-mq})\overline{Pd\{Ph_2PCH(AuPPh_3)C(O}Ph\}BF_4$ (**8**) in which the electrophilic fragment $[Au(PPh_3)]^+$ is attached to the carbon atom of the enolate moiety.

## Introduction

Metal enolates are extensively used in metal-mediated organic synthesis.[2] Their reactivity is dominated by the ambidentate nature of this reagent, but it is only recently that the direct observation of both O- and C-bound forms of an enolate (of Ru) was reported.[3] The study of naked enolates allows interesting comparisons to be made on the influence of ion-pairing effects on their reactivity,[4] whereas ambident reactivity has also been studied in the gas phase.[5] Obviously, structural information about metal enolates obtained by X-ray diffraction is valuable owing to its importance in understanding the chemical and stereochemical reactivity of these reagents.[6] Prior to this study, we investigated the synthesis and reactivity of transition metal complexes of $\alpha$-phosphino enolates of the type [Ph$_2$-

---

[†] Université de Lausanne.

[‡] Università di Parma.

[§] Laboratoire de Chimie Quantique, Université Louis Pasteur.

[∥] Laboratoire de Chimie de Coordination, Université Louis Pasteur.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) This article may be considered as part 24 in the series Complexes of Functional Phosphines. For part 23, see: Braunstein, P.; Kelly, D. G.; Dusausoy, Y.; Bayeul, D.; Lanfranchi, M.; Tiripicchio, A. *Inorg. Chem.*, in press.

(2) (a) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: New York, 1982. (b) Nakahira, H.; Ryu, I.; Ikebe, M.; Kambe, N.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 177. (c) Heathcock, C. H. *Aldrichim. Acta* **1990**, *23*, 99. (d) Evans, D. A.; Rieger, D. L.; Bilodeau, M. T.; Urpi, F. *J. Am. Chem. Soc.* **1991**, *113*, 1047. (e) Denmark, S. E.; Henke, B. R. *J. Am. Chem. Soc.* **1991**, *113*, 2177. (f) Heeres, H. J.; Maters, M.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1992**, *11*, 350.

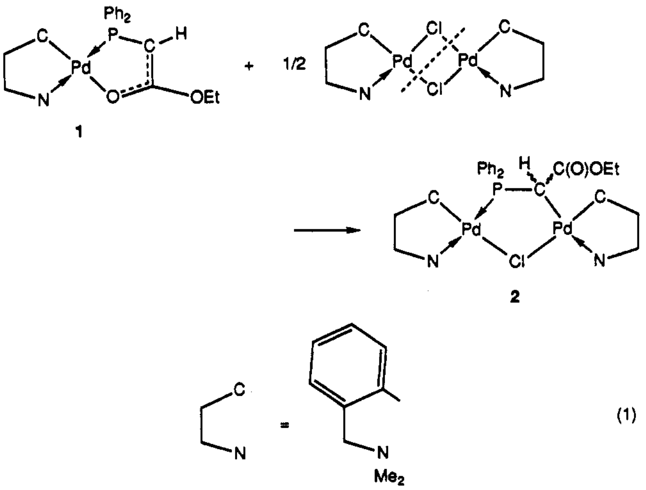
(3) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670.

(4) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1991**, *10*, 1652.

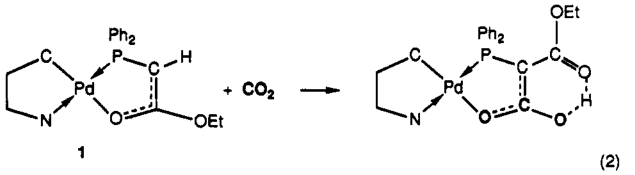
(5) Freriks, I. L.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 9119.

0276-7333/93/2312-4359$04.00/0

$\mathrm{PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)(OEt)]^-}$.[1,7] In these complexes, a metal–phosphorus bond is always present and helps maintain the enolate functionality close to the metal center. The known ambidentate nature of organic enolates is reflected in these complexes by the occurrence of metal–oxygen or metal–carbon bonds. That the chelating (*P,O*) form may be converted to a *μ*-(*P,C*) form was demonstrated by the reaction of eq 1.[7] The presence in such phosphino enolates of three functionalities (P, C, and O) available for potential bonding to one or more metal centers makes them particularly interesting reagents and allows detailed investigations of the selectivity and possible interconversions of the metal–ligand interactions. Addition of an unsaturated 14e fragment $[(\overline{\mathrm{C\,N}})\mathrm{Pd}]^+$ to 2 afforded $[\{(\overline{\mathrm{C\,N}})\mathrm{Pd}\}_3\{\mu_3\text{-}\mathrm{Ph_2}P\mathrm{CH\overset{\cdot\cdot\cdot}{-}C)(\overset{\cdot\cdot\cdot}{-}}O\mathrm{)OEt}\}(\mu_3\text{-OH})]$ in which all three donor atoms are bonded to palladium centers.[8] We have been interested in comparing the reactivity of various enolate complexes as a function of the transition metal and of the substituents on the enolate moiety. The nucleophilicity of the enolate carbon in 1 has been previously evidenced by reactions of this complex with electrophiles such as $CO_2$ (eq 2),[7] organic isocyanates,[9] or activated alkynes.[10] This reactivity is markedly reduced in the corresponding keto enolate complexes, and 3 does not react with $CO_2$ under similar conditions (room temperature, atmospheric pressure). This was accounted for by the decrease in electron density within the enolate moiety, and in particular at the $C_\alpha$ carbon, as a result of the replacement of the electron donating ethoxy group by a phenyl substituent.[11] However, we shall see below that the residual nucleophilicity of the $C_\alpha$ carbon in a palladium complex similar to 3 is sufficient to give rise to reaction with the more reactive electrophile $[Au(PPh_3)]^+$.



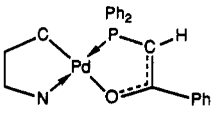
(1)



(2)

**Table I. Selected Bond Distances (Å) and Angles (deg) for Complex 4**

| | | | |
|---|---|---|---|
| K–O1 | 2.840(5) | P–C21 | 1.857(3) |
| K–O2 | 2.981(5) | P–C31 | 1.860(2) |
| K–O3 | 2.810(4) | P–C37 | 1.783(5) |
| K–O4 | 2.957(5) | O7–C38 | 1.270(6) |
| K–O5 | 2.873(4) | C37–C38 | 1.366(6) |
| K–O6 | 2.972(4) | C38–C41 | 1.530(6) |
| K–O7 | 2.631(4) | | |
| C31–P–C37 | 104.7(2) | P–C37–C38 | 120.7(3) |
| C21–P–C37 | 101.6(2) | O7–C38–C37 | 126.0(4) |
| C21–P–C31 | 99.2(1) | C37–C38–C41 | 118.2(3) |
| K–O7–C38 | 121.3(3) | O7–C38–C41 | 115.8(4) |



3

Somewhat surprisingly, the alkali metal salts of $\mathrm{[Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-})(OEt)]^-}$ or $\mathrm{[Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)Ph]^-}$ did not react either with $CO_2$ under conditions where the corresponding palladium(II) phosphino enolate complexes 1 reacted readily or with other electrophiles (see Experimental Section). In order to rationalize these differences in reactivity and gain a better insight into the metal–enolate interactions, we decided to isolate and structurally characterize potassium salts of $\mathrm{[Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)Ph]^-}$ in which the cation could interact with the anion or be completely separated as a cryptate. *Ab initio* SCF calculations on the free phosphine enolate anion and on the $Li^+$ and $Na^+$ complexed phosphine enolate were also carried out.

## Results and Discussion

**Synthesis and Structure of Potassium Phosphino Enolates.** The complexes $\mathrm{[K(18\text{-}crown\text{-}6)][Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)Ph]}$ (**4**), $\mathrm{[K(Kryptofix\text{-}2,2,2)][Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)Ph]}$ (**5**), and $\mathrm{[K(18\text{-}crown\text{-}6)][Ph_2PCH\overset{\cdot\cdot\cdot}{-}C(\overset{\cdot\cdot\cdot}{-}O)OEt]}$ (**6**) were prepared by deprotonation of the neutral phosphine ligands and isolated as described in the Experimental Section. The molecular structures of complexes **4** and **5** were determined by X-ray diffraction and selected bond distances and angles are given in Tables I and II, respectively. In the structure of complex **4** there are discrete molecules (Figure 1) where the oxygen atom from the phosphino enolato ligand interacts with the potassium ion at a distance of 2.631(4) Å. This value is shorter than the K–O values involving the ether molecule which range from 2.811(4) to 2.981(5) Å. The direction of the K–O7 bond forms an angle of 34.0(1)° with the normal to the mean plane passing through the ether oxygens from which potassium protrudes by 0.880(1) Å. The six oxygen

---

(6) (a) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 8602. (b) Maetzke, T.; Seebach, D. *Organometallics* **1990**, *9*, 3032. (c) Veya, P.; Floriani, C.; Chiesi-Villa, Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1166. (d) Etter, M. C.; Ranawake, G. *J. Am. Chem. Soc.* **1992**, *114*, 4430.

(7) (a) Braunstein, P.; Matt, D.; Fischer, J.; Mitschler, A.; Ricard, L. *Nouv. J. Chem.* **1980**, *4*, 493. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(8) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410.

(9) (a) Bouaoud, S. E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *J. Chem. Soc., Chem. Commun.* **1987**, 488. (b) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279. (c) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.

(10) (a) Balegroune, F.; Braunstein, P.; Gomes Carneiro, T. M.; Grandjean, D.; Matt, D. *J. Chem. Soc., Chem. Commun.* **1989**, 582. (b) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *Organometallics* **1989**, *8*, 1737.

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

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

| | | | |
|---|---|---|---|
| K–O1 | 2.899(4) | K–N1 | 2.997(7) |
| K–O2 | 2.802(4) | K–N2 | 2.998(7) |
| K–O3 | 2.851(7) | O7–C38 | 1.268(6) |
| K–O4 | 2.770(4) | C37–C38 | 1.404(9) |
| K–O5 | 2.813(6) | C38–C41 | 1.517(8) |
| K–O6 | 2.813(4) | | |
| C31–P–C37 | 102.7(2) | O7–C38–C37 | 126.2(5) |
| C21–P–C37 | 104.5(2) | C37–C38–C41 | 118.5(5) |
| C21–P–C31 | 96.6(2) | O7–C38–C41 | 115.2(5) |
| P–C37–C38 | 120.7(4) | | |

atoms surround the potassium ion up and down with respect to the mean plane in a range from −0.237(4) to +0.286(4) Å. The bond distances and angles within the P, C37, C38, O7 system are consistent with some π delocalization leaving a significant double bond character for the C37–C38 bond [1.366(6) Å]. Accordingly, the system is nearly planar, as indicated by the value of the P–C37–C38–O7 torsion angle [−4.4(6)°]. The P···O7 distance [3.066(5) Å] corresponds well to a possible "bite" distance. The P, C37, C31 plane forms a dihedral angle of 72.6(2)° with the O7–C38–C37–P plane, indicating the phosphorus lone pair to lie nearly in the latter plane. The C41···C46 phenyl ring is tilted by 30.7(1)° with respect to the O7–C38–C37–P plane. Crystal packing is mainly determined by a contact less than 3.5 Å running parallel to [010] [C45···O2′ = 3.370(4) Å (′ = $x, y + 1, z$)].

The structure of complex 5 consists of complexed cations and anions linked by a weak C17···O7 interaction which could be interpretable as a hydrogen bond: C17···O7 = 3.332(7) Å, C17–H17B···O7 = 168.7°, H17B···O7 = 2.26 Å, H17B···O7···C38 = 134.5° (Figure 2).[12a] The geometry of the cryptated $K^+$ ions is normal with K···O (in the range 2.770(4)–2.899(4) Å) and K···N distances [mean value 2.998(7) Å] comparable to those observed, *e.g.*, in potassium cryptand[2.2.2] electride.[12b] The geometry of the anion is close to that observed in complex 4, the main difference being due to the significant lengthening of the C37–C38 bond distance [1.404(9) Å]. The lengthening along with a more consistent planarity of the O7–C38–C37–P system [torsion angle around C38–C37 being −1.3(9)°] indicates a more pronounced π delocalization for the free ligand. The phosphorus lone pair lies nearly in the plane O7–C38–C37–P as indicated by the dihedral angle between P, C21, C37 and O7–C38–C37–P [72.9(2)°]. The C41···C46 phenyl ring is tilted by 29.3(2)° with respect to the latter plane. The P···O7 separation is 3.090(5) Å. There are no significant intermolecular contacts.

**Reactivity Studies.** Three important factors are known to govern the reactions of enolates with carbonyl compounds in aldol-type reactions: (a) the nucleophilicity of the enolate which is related *inter alia* to its composition, structure, and steric properties; (b) the electrophilic activation of the carbonyl compound by the metal center, which may or may not be a transition element; (c) the substrate orientation in the transition state which is tuned by the metal. Modifications of the metal center or of its coordination sphere could therefore lead to changes in the reactivity of the system. We have observed that, unlike 1, the enolate complexes 4 and 6 do not react with $CO_2$ (eq 3; R = Ph, OEt): they are recovered from a $CO_2$-saturated tetrahydrofuran solution and no gas absorption was observed. That the enhanced nucleophilicity of the enolate resulting from complexation by 18-crown-6 of the potassium counterion is not sufficient to lead to reaction indicates that this is probably due to the inability of the latter to govern the reaction (see points a and b, above). The coordination sites around the cation are occupied, and the electrophilic activation of the substrate becomes impossible. Access to an open transition state is disfavored (eq 4). Noyori *et al.* have made related observations with naked enolates.[13] They found that reaction with benzaldehyde is reversible and endothermic, illustrating the role of the metal as a driving force for the reaction (eqs 5 and 6). Since $CO_2$ is not as strong an electrophile as benzaldehyde, it is not too surprising then that if the benzaldehyde reaction is reversible, no reaction occurs with $CO_2$. The benzaldehyde reaction remains reversible as long as an electrophile has not been added to the reaction mixture. We have not added a Lewis acid in our case to confirm this observation.

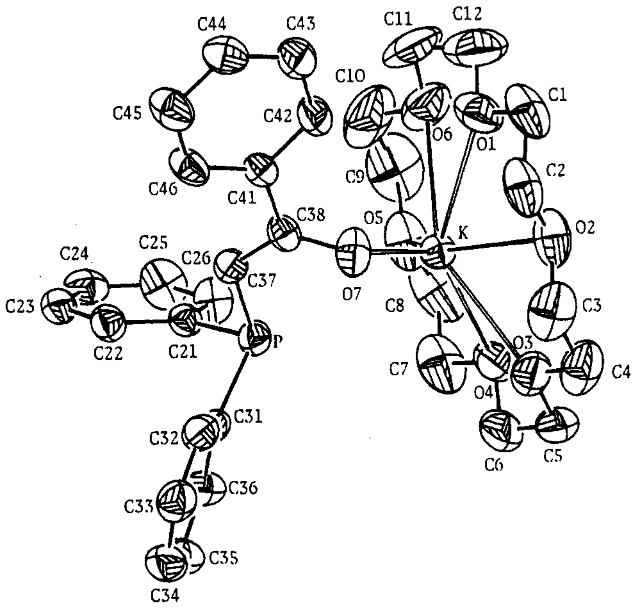
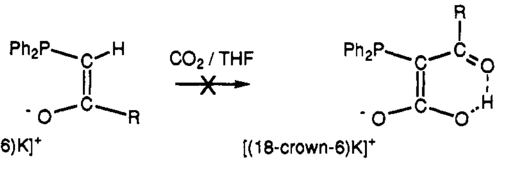
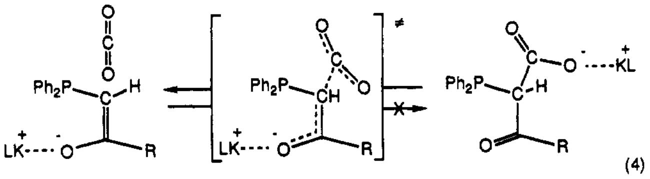


**Figure 1.** ORTEP drawing of complex 4 (30% probability ellipsoids).



(3)



(4)

As found in the case of 1, no reaction was observed between 4 or 6 and diphenylacetylene: 4 was recovered after 12 h of reaction in toluene at 70 °C, and although the orange color of 6 had turned yellow after addition of diphenylacetylene, mostly 6 was recovered and identified. The $^1H$ NMR spectrum suggests the presence of two

---

(12) (a) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.* 1984, *B40*, 159–165. (b) Ward, D. L.; Huang, R. H.; Dye, J. L. *Acta Crystallogr.* 1988, *C44*, 1374–76.

(13) (a) Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223. (b) Noyori, R.; Nishida, I.; Sakata, J. *Ibid.* **1981**, *103*, 2106.

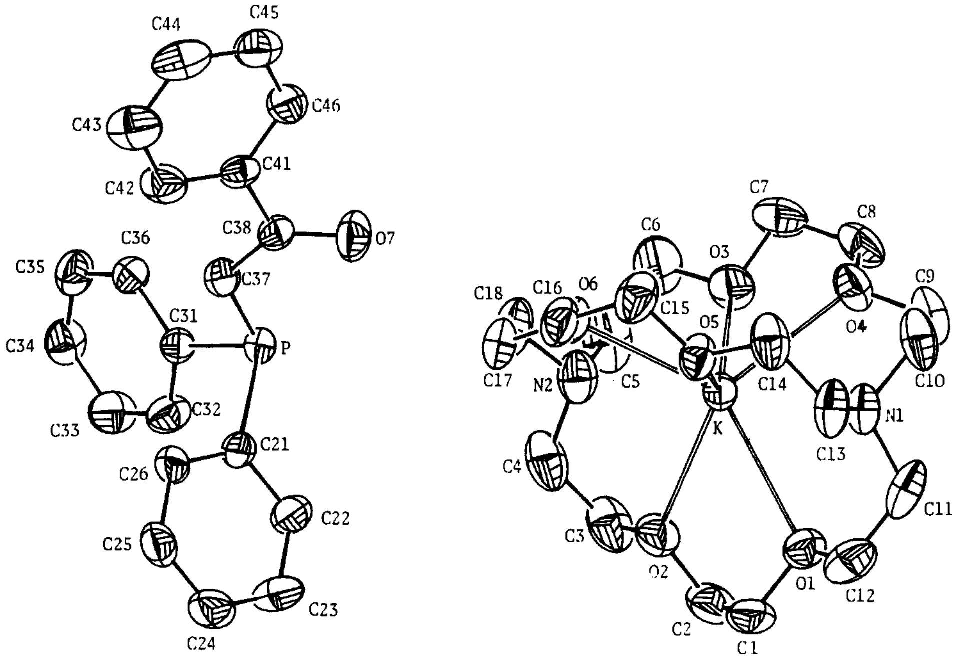
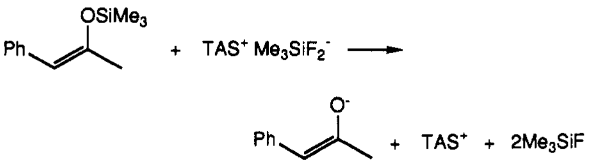
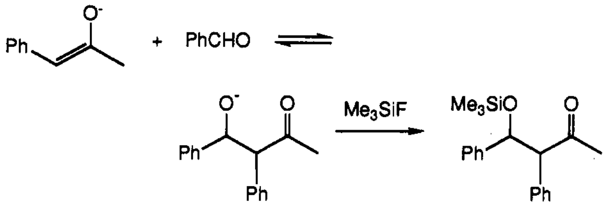


**Figure 2.** ORTEP drawing of complex **5** (30% probability ellipsoids).



(5)

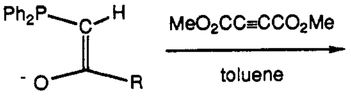


(6)

$TAS^+ = (Et_2N)_3S^+$

species, in a 4:1 ratio. The major one is **6** whereas the minor one, which has not be identified, shows a $J$(PH) coupling constant of 24.5 Hz against 7.5 Hz in **6**.

With the activated alkyne dimethyl acetylenedicarboxylate (DMAD), a reaction was observed with **4**, but it is not selective. The enolate appears to react on the ester carbonyl function as well as on the carbon–carbon triple bond. During workup, a decomposition or hydrolysis product was isolated (eq 7) and structurally characterized as **7**.[14] The other product(s) could not be identified by IR or $^1$H NMR.



$[(18\text{-crown-6})K]^+$

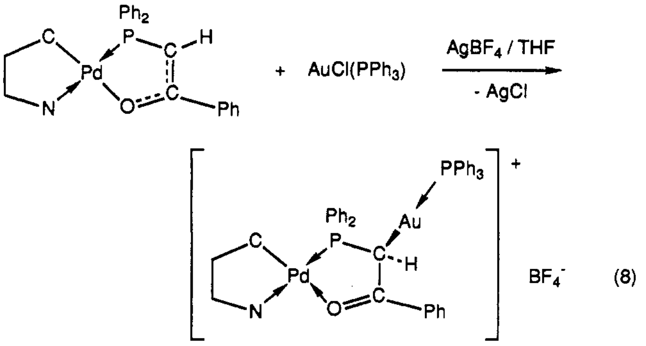
**4**

(?) + $Ph_2P(O)O^- K^+(18\text{-crown-6})$ (7)

**7**

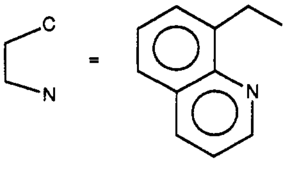
Although **6** appears more reactive than **4**, which parallels the behavior of **1** vs **3**, the reactivity of these phosphino enolates seems to be strongly influenced by the nature and structure of the countercation, which alters the nucleophilicity of the enolate. The complexed potassium cation cannot participate significantly in substrate activation, and when the electrophile is sufficiently reactive (DMAD), it cannot direct the regioselectivity.

Having observed that the enolate moiety of **3** is easily protonated, affording the keto phosphine cationic complex $[(C\ N)Pd\{Ph_2PCH_2C(O)Ph\}]^+$ (CH N = dimethylbenzylamine or 8-methylquinoline), we reacted the related palladium(II) phosphino enolate complex (8-mq)Pd[Ph$_2$PCH$\cdots$C($\cdots$O)Ph] (8-mqH = 8-methylquinoline) in THF with AuCl(PPh$_3$) in the presence of AgBF$_4$. It afforded the bimetallic complex [(8-mq)Pd{Ph$_2$PCH(AuPPh$_3$)C(O)Ph}]BF$_4$ (**8**) in which the electrophilic fragment [Au(PPh$_3$)]$^+$, isolobal with the proton, is attached to the newly chiral C$_\alpha$ carbon atom of the former enolate moiety (eq 8). The structure drawn for **8** is supported by



(8)

**8**



---

(14) Unpublished results.

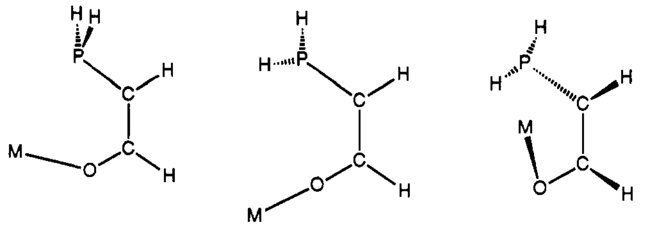
the analytical and spectroscopic data.[41] In particular, the $^{31}P\{^1H\}$ NMR spectrum consists of an AB pattern with a $^3J(P_{Pd}P_{Au})$ value of 11.6 Hz. The $^1H$ NMR resonance for the PCH proton occurs at $\delta$ 5.26 as a triplet, owing to a accidental equal coupling to both phosphorus atoms. The $^2J(PH)$ value of 8.4 Hz compares with that found in $[(8\text{-mq})Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$.[11] Although the enolate absorption of $(8\text{-mq})Pd[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]$ at 1474 cm$^{-1}$ is no longer present in the infrared spectrum of 8, it is surprising that the latter does not contain a $\nu(C{=}O)$ band around 1570 cm$^{-1}$, as expected by analogy with the cationic complex $[(8\text{-mq})Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$. It is interesting that the excess of electron density in bis(diphenylphosphino)methanide complexes has been used recently to form C—Au bonds with $[Au(PPh_3)]^+$.[15]

These results show that when the phosphino keto enolate ligand $[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]^-$ is coordinated to Pd(II), the residual nucleophilicity of the $C_\alpha$ carbon is not sufficient to give rise to a reaction with $CO_2$ but allows formation of a gold–carbon bond with the stronger electrophile $[Au(PPh_3)]^+$. Obviously, coordination of the phosphino enolates, as in **1** or **3**, plays a key role in directing their reactivity. This has been rationalized on the basis of *ab initio* SCF calculations.

**Theoretical Studies.** *Ab initio* SCF calculations[16] on the free phosphine enolate anion and on the $Li^+$ and $Na^+$ complexed phosphine enolate were carried out in order to rationalize the observed structures and to try to account for the reactivity pattern of such systems toward electrophiles and, more specifically, toward carbon dioxide. For this purpose a comparison was also made with the previously synthesized palladium phosphino enolate complex.[7]

Three possible geometries denoted **I–III** in Chart I were investigated for the Li and Na systems and the most important geometrical parameters optimized by using the nonpolarized basis set. Single point energy determinations using the polarized basis set were also performed for the Li phosphine enolate complexes. Table III summarizes the computed energy values.

**Chart I**



I II III

**Table III. Total and Relative Energies[a] (in Parentheses) of the Three Various Geometries Investigated for the $M[PH_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O)H]$ System (M = Li, Na)**

| | I | II | III |
|---|---|---|---|
| Li, BS I[b] | −500.5422 (0) | −500.5267 (+9.7) | −500.5114 (+19.3) |
| Li, BS II | −500.6499 (0) | −500.6278 (+13.9) | −500.6267 (+14.6) |
| Na, BS I | −654.7289 (0) | −654.7112 (+11.1) | −654.7051 (+14.9) |

[a] The total energies are in atomic units (au), and the relative energies in kcal/mol. [b] BS I denotes the nonpolarized basis set, and BS II the polarized one.

In the three structures the C–P, $C_\alpha$–$C_\beta$, and C–O bond lengths were set at 1.78, 1.38 and 1.29 Å, respectively (on the basis of the X-ray crystal structure of the title compound and other related X-ray crystal data[23]). The C–C–H angles and the C–H bond lengths were set at the standard values of 120° and 1.10 Å, respectively. Structure **I** is characterized by a $PH_2$ moiety oriented to have its phosphorus lone pair in the C–C–C–O plane. In this structure the C–C–P and the pyramidalization angle at the phosphorus were optimized at 119.8 and 116.2°, respectively. The Li–O distance was optimized to 1.73 Å. Most noticeably, the optimized value of the Li–O–$C_\beta$ angle was found to be 129.6°. This quite acute angle is traced to a dual interaction of $Li^+$ with both an oxygen lone pair and the phosphorus lone pair. A similar value (130.2°) has been also found for the $Na^+$ complex. The computed geometry of **I** is in agreement with the X-ray crystal structure of the title compound and of known Li enolate structures.[23] It has, however, a rather long Li–O bond length, longer at least than the one obtained in similar calculations for the lithium enolate of acetaldehyde.[24,25] The rationale lies in the above mentioned dual interaction of the lithium atom: In the calculations of the lithium enolate of acetaldehyde there is also a lengthening of the Li–O bond when Li has a bridging character.[24,25] Moreover in **II**, where the Li atom is bound to the oxygen atom only, the Li–O bond is shorter; *vide infra*. This second structure was considered in order to check the influence of the conjugation between the phosphorus lone pair and the $\pi$ system of the enolate moiety. Most of the geometrical parameters of **I** were kept. The optimization was performed on the most critical parameters, i.e. the Li–O–C angle, the pyramidalization angle at phosphorus, and the Li–O bond length, yielding values of 174.5°, 117.7°, and 1.64 Å, respectively. The decrease of the Li–O bond length and the quasi linearity of the Li–O–C arrangement are well indicative of the loss of the interaction between $Li^+$ and the phosphorus lone pair. In fact, this loss is one of the two contributors to the destabilization of **II** (13.9 kcal/mol with the polarized basis set; see Table III); the other one is the destabilization of the HOMO of the system which

---

[15] Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez de Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3365 and references cited therein.

[16] The calculations were carried out with the Asterix system of programs[17] using the following Gaussian basis sets: (9,5) and (11,7) contracted to [3,2] and [4,3] for the first and second row atoms, respectively,[18] and (4) contracted to [2] for hydrogen.[19] In some instances d polarization functions were added with an exponent of 0.55 for the phosphorus atom and 0.8 for the carbon and oxygen atoms. The Pd atom used a (16,11,9) Gaussian basis set contracted to [7,5,5].[20]

[17] (a) Ernenwein, R.; Rohmer, M.-M.; Bénard, M. *Comput. Phys. Commun.* **1990**, *58*, 305. (b) Rohmer, M.-M.; Demuynck, J.; Bénard, M.; Wiest, R. *Comput. Phys. Commun.* **1990**, *60*, 127. (c) Wiest, R.; Demuynck, J.; Bénard, M.; Rohmer, M.-M.; Ernenwein, R. *Comput Phys. Commun.* **1991**, *62*, 107.

[18] Huzinaga, S. Technical Report, University of Alberta, Edmonton, Alberta, Canada, 1971.

[19] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

[20] The original (15,9,8) basis set[21] was modified by the addition of an s primitive of exponent 0.3056 to suppress the gap between the functions needed to describe the widely separated 4s and 5s shells, two p functions of exponents 0.2356 and 0.083 86 to describe the 5p shell, and one d function of exponent 0.078 90. These exponents were chosen according to the even tempered criterion.[22]

[21] Veillard, A.; Dedieu, A. *Theor. Chim. Acta* **1984**, *65*, 215.

[22] Raffenetti, R.; Bardo, R. D.; Ruedenberg, K. In *Energy Structure and Reactivity*; Smith, D. W., McRae, W. B., Eds.; Wiley: New York, 1973; p 164.

[23] (a) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3345; **1986**, *108*, 462. (b) Maetske, T.; Hidber, C. P.; Seebach, D. *J. Am. Chem. Soc.* **1990**, *112*, 8248. (c) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403.

[24] Lynch, T. J.; Newcomb, M.; Bergbreiter, D. E.; Hall, M. B. *J. Org. Chem.* **1980**, *45*, 5005.

[25] Leung-Toung, R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 1042.

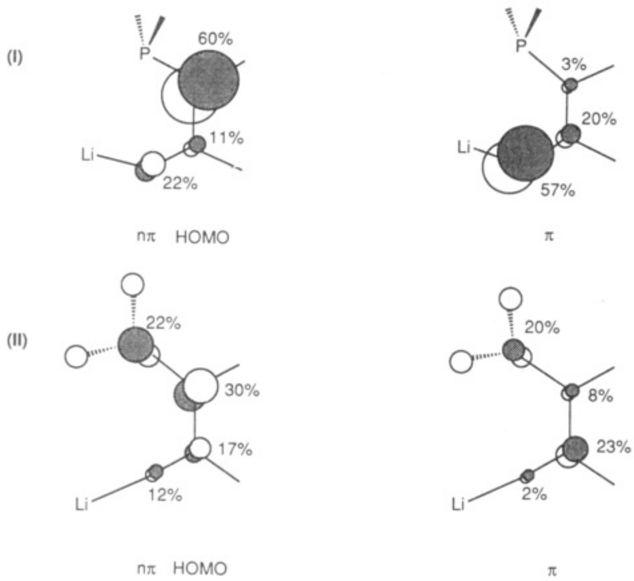


**Figure 3.** Allylic-type $\pi$ orbitals of the P–C–C–O unit in the geometries **I** and **II** of the $\mathrm{Li[PH_2CH{\cdots}C({\cdots}O)H]}$ system.

becomes quite appreciably P–C antibonding; see Figure 3. Structure **III** was finally designed to allow the interaction of the lithium 2s orbital with both the oxygen atom lone pairs and the $\pi$ orbital of the carbon–carbon bond. It was derived from a structure computed to be the most stable one for $LiOCHCH_2$, the lithium enolate of acetaldehyde.[24] But, as seen in Table III, **III** turned out to be much less stable than **I**. Here too the loss of the interaction between the phosphine lone pair and the $Li^+$ empty 2s orbital is one of the factors which account for this destabilization.

The $\pi$ type orbitals are quite similar in the free enolate anion (which is best relevant to the experimental system where the cation has been complexed by the crown ether), in the alkali metal complexes (in their ground state structure **I**), and in the Pd complex. More specifically, the HOMO (which corresponds to the nonbonding orbital of an allylic system) is highly localized on the $C_\alpha$ atom: see for instance Figure 3 where it is displayed for structure **I**. The weight of the $C_\alpha$ atom in the HOMO is about the same in all systems: it amounts to 62% in the free enolate anion, 60% in the Li complex, and 61% in both the Na and Pd complexes. Conversely, the $\pi_{C-C-O}$ bonding orbital which lies at lower energy is localized on the oxygen atom, and its distribution is more counterion dependent (the weight of the oxygen atom amounts to 50% in the free enolate anion but rises to 57% in the Li system and 58% in the Na system and is only 49% in the Pd complex). That in the Pd complex the HOMO is largely localized on the $C_\alpha$ atom and that the $\pi_{C-C-O}$ orbital is more spread out on the three atoms is in line with the observed nucleophilic character of the $C_\alpha$ atom with $CO_2$ as an electrophile.[7] On the basis of the above results the free enolate ion and the enolate ion complexed by a crown ether should behave similarly. On the other hand, the Li or Na complex with a $\pi_{C-C-O}$ orbital more localized on the oxygen atom may give rise to a less clear-cut regioselectivity. Indeed, theoretical[25] and experimental[26] studies of the addition of ketenes—which are close analogs of $CO_2$—to enolates point to a subtle kinetic balance between O-acylation and C-acylation, although the C-acylated products are thermodynamically preferred.

**Table IV. Reaction Enthalpies (As Obtained from the Calculations with the Polarized Basis Set) for the Reaction $\mathbf{M[PH_2CH{\cdots}C{\cdots}O)R] + CO_2 \rightarrow M\{PH_2C[C(O)R]{\cdots}C({\cdots}O)OH\}}$**[a]

| | M = Li | M = Pd(NH₃)(CH₃) |
|---|---|---|
| R = H | +6.0 (−8.3) | +4.8 (−12.2) |
| R = OH | −1.7 (−20.3) | −7.8 (−24.8) |

[a] In kcal/mol. The values in parentheses refer to the unpolarized basis set.

The effect of the substitution at the $C_\beta$ atom of an alkyl group by an alkoxy group was modeled in the Li and Pd phosphine enolate systems by the replacement of H by OH (in the experimental palladium complex the $C_\beta$ atom is bound to an ethoxy ligand). The major change occurring upon this substitution is again found in the HOMO where the weight of the $p_z$ orbital on the $C_\alpha$ atom increases to 65% in the Li system and to 67% in the Pd system.[27] The highest localization of the HOMO in this latter case may well explain the high reactivity with carbon dioxide which was experimentally found.[7]

The values computed for the enthalpy of the reaction $\mathrm{M[PH_2CH{\cdots}C({\cdots}O)R] + CO_2 \rightarrow M\{PH_2C[C(O)R]{\cdots}C({\cdots}O)OH\}}$ (M = Li, $Pd(NH_3)(CH_3)$; R = H, OH) seem to confirm this feature (see Table IV). The reaction is exothermic for R = OH and endothermic for R = H (polarized basis set calculations). Moreover the greatest exothermicity is found for the palladium system.[28,29] Therefore in addition to kinetic arguments (which are based on the high polarization of the HOMO on the $C_\alpha$ atom) the thermodynamic data account for the fact that an insertion of $CO_2$ is found in the Pd case in contrast with the Li case. More theoretical work is of course needed to determine the structure and energetics of the transition state in each of these reactions, especially in the Pd case. Using again the analogy of ketene addition to the lithium enolate of acetaldehyde,[25] one possibility would be a structure characterized by the coordination of Li to two oxygen atoms, one from the enolate ligand and one from the incoming carbon dioxide; see **IV**. This is of course a favorable interaction from the electrostatic point of view and it may well drive the C–C coupling process. One has to be aware however of the presence, in this square planar $d^8$ metal complex, of a doubly occupied $d_{z^2}$ orbital. This orbital may experience a repulsive interaction with the $n\pi CO_2$ orbital which is also doubly occupied; see **V**. An alternative to this approach on $C_\alpha$ would be an electrophilic attack of $CO_2$ on the Pd atom itself. This type of attack would be driven by a two electron stabilizing interaction between the $d_{z^2}$ orbital and the empty $\pi^* CO_2$ orbital (see **VI**), and indeed such an interaction has been put forth to explain the $\eta^1$ coordination mode of $CO_2$ in square planar

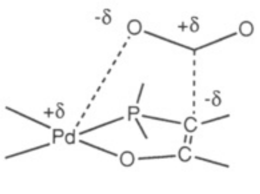
---

(26) Gong, L.; Leung-Toung, R.; Tidwell, T. T. *J. Org. Chem.* **1990**, *55*, 3634.

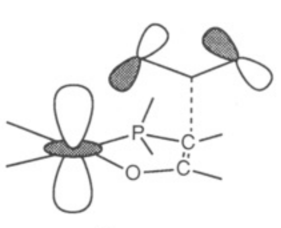
(27) Similar features were found in the polarized basis set calculations.

(28) The total energies with the polarized basis set are (in au) as follows: $\mathrm{Li[PH_2CH{=}C(O)H]}$, −500.6499; $\mathrm{Li\{PH_2C[C(O)H]{=}C(O)OH\}}$, 688.1781; $\mathrm{Li[PH_2CH{=}C(O)OH]}$, −575.4946; $\mathrm{Li\{PH_2C[C(O)OH]{=}C(O)OH\}}$, −763.0351; $CO_2$, −187.5378; $\mathrm{Pd(NH_3)(CH_3)[PH_2CH{=}C(O)H]}$, −5516.3422; $\mathrm{Pd(NH_3)(CH_3)\{PH_2C[C(O)H]{=}C(O)OH\}}$, −5703.8724; $\mathrm{Pd(NH_3)(CH_3)[PH_2CH{=}C(O)OH]}$, −5591.1855; $\mathrm{Pd(NH_3)(CH_3)\{PH_2C[C(O)OH]{=}C(O)OH\}}$, −5778.7358.

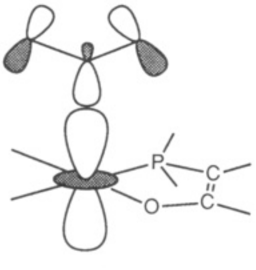
(29) For the non-polarized basis set the respective values are as follows: $\mathrm{Li[PH_2CH{=}C(O)H]}$, −500.5422; $\mathrm{Li\{PH_2C[C(O)H]{=}C(O)OH\}}$, −687.9660; $\mathrm{Li[PH_2CH{=}C(O)OH]}$, −575.3489; $\mathrm{Li\{PH_2C[C(O)OH]{=}C(O)OH\}}$, −762.7917; $CO_2$, −187.4105; $\mathrm{Pd(NH_3)(CH_3)[PH_2CH{=}C(O)H]}$, −5516.2194; $\mathrm{Pd(NH_3)(CH_3)\{PH_2C[C(O)H]{=}C(O)OH\}}$, −5703.6493; $\mathrm{Pd(NH_3)(CH_3)[PH_2CH{=}C(O)OH]}$, −5591.0263; $\mathrm{Pd(NH_3)(CH_3)\{PH_2C[C(O)OH]{=}C(O)OH\}}$, −5778.4763.



IV



V



VI

Rh(I) carbon dioxide complexes.[30] However, the electrostatics would now run against this alternative. Very preliminary calculations, carried out at the SCF level and using frozen geometries, seem to indicate that the former pathway is slightly preferred. One will need to carry out a geometry optimization procedure and to include the electron correlation effects (which are expected to be nonnegligible[25,30]) to put this conclusion on a more firm basis. Work along these lines is now in progress.

## Experimental Section

**General Data.** All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium benzophenone–ketyl; pentane and hexane from sodium; dichloromethane over $P_2O_5$. Nitrogen (Air Liquide R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. Infrared spectra were recorded in the region 4000–400 cm$^{-1}$ on a Perkin-Elmer 398 spectrophotometer or on a Bruker IFS-66 instrument. The $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded at 200.13 and 81.02 MHz, respectively, on a FT-Bruker WP 200 SY instrument. Chemical shifts, in ppm, are positive downfield relative to external $Me_4Si$ for $^1$H NMR and to external 85% $H_3PO_4$ in $H_2O$ for $^{31}$P NMR spectra. $Ph_2PCH_2C(O)Ph$[11] was prepared according to the literature, and 18-crown-6 and Kryptofix-2,2,2 (Aldrich) were used as received.

**[K(18-crown-6)][Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)Ph] (4).** $Ph_2PCH_2C(O)Ph$ (2.45 g, 8.0 mmol) was added to a suspension of KH (0.34 g, 8.5 mmol) in THF (50 mL), and the reaction mixture was stirred for 2 h. After addition of 18-crown-6 (2.07 g, 8.0 mmol) the solution was stirred for a few minutes. The solvent was removed under reduced pressure, and the yellow oil was treated with diethyl ether (50 mL). A yellow, microcrystalline solid formed which was filtered and dried under vacuum (3.85 g, 80%). X-ray quality crystals were obtained by extraction with diethyl ether. Anal. Calcd for $C_{32}H_{40}KO_7P$ ($M$ = 606.76): C, 63.35; H, 6.65. Found: C, 63.12; H, 6.62. $^1$H NMR ($C_6D_6$): $\delta$ 3.17 (s, 24H, $OCH_2$), 5.22 (d, 1H, $J_{HP}$ = 4.5 Hz, =CH), 7.1–7.4 (m, 10H, PPh), 7.9 (m, 3H, Ph), 8.4 (m, 2H, Ph). $^{13}$P{$^1$H} NMR ($C_6D_6$): $\delta$ −23.4 (s). $^{13}$C NMR ($C_6D_6$): $\delta$ 70.7 (s, $OCH_2$), 75.0 (d, $J_{CP}$ = 15.2 Hz, =CH), 127–129 (m, Ph), 134 (d, Ph), 148.4 (s, Ph), 178.1 (d, =C-O).

**[K(Kryptofix-2,2,2)][Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)Ph] (5).** Solid $Ph_2PCH_2C(O)Ph$ (3.13 g, 3.24 mmol) was added to a suspension of KH (0.13 g, 3.24 mmol) in THF (30 mL) and the reaction mixture was stirred for 1 h. Kryptofix-2,2,2 (1.00 g, 2.66 mmol) was added, and after stirring for a few minutes, the solvent was removed under vacuum and the yellow oil treated with diethyl ether (50 mL). Yellow crystals were formed by extraction with ether within a night. These were filtered, dried, and collected (1.37 g, 72%). Anal. Calcd for $C_{38}H_{52}KN_2O_7P$ ($M$ = 718.93): C, 63.49; H, 7.29; N, 3.90. Found: C, 63.47; H, 7.65; N, 3.78. $^1$H NMR ($C_6D_6$): $\delta$ 2.27 (t, $J_{HH}$ = 4.5 Hz, 12H, $NCH_2$), 3.23 (t, $J_{HH}$ = 4.75 Hz, 12H, $OCH_2$), 5.15 (d, $J_{HP}$ = 4.6 Hz, 1H, =CH—P), 7.1–7.4 (m, 10H, PPh), 8.0 (m, 3H, Ph), 8.4 (m, 2H, Ph). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ −22.6 (s). $^{13}$C NMR ($C_6D_6$): $\delta$ 56.0 (s, $NCH_2$, Kryptofix-2,2,2), 69.0 (s, $OCH_2$, Kryptofix-2,2,2), 71.2 (s, $OCH_2$, Kryptofix-2,2,2), 75.3 (d, $J_{CP}$ = 10.9 Hz, =CH), 126.7–134.1 (s, Ph), 149.2 (d, Ph).

**$Ph_2PCH_2C(O)OEt$.** This ligand has been described previously.[31] A modified procedure using $LiPPh_2$ prepared *in situ* is as follows. Lithium sand (1.07 g, 154.0 mmol) was added to a solution of $PPh_3$ (20.2 g, 77.0 mmol) in THF (250 mL), and the reaction mixture was stirred overnight. Anhydrous $NH_4Cl$ (4.12 g, 77.0 mmol) was added to the orange solution to eliminate the phenyllithium formed and the reaction mixture was vigorously stirred for 1 day. This $LiPPh_2$ solution was then added dropwise at −40 °C over 1.5 h to a solution of $ClCH_2C(O)OEt$ (9.5 mL, 77.0 mmol) in THF (150 mL). The reaction mixture was stirred and the temperature allowed to rise rapidly. Evaporation to dryness left a residue which was extracted with ether (200 mL); the LiCl was filtered out and washed with ether (3 × 150 mL). The ether was then removed under reduced pressure, and the solution was distilled under reduced pressure (150–155 °C/1 Torr). A colorless liquid was collected (13.5 g, 64%). IR (neat): $\nu$(C=O) 1730 (s) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.26 (t, $J_{HH}$ = 7.2 Hz, 3H, $CH_3$), 3.13 (s, 2H, $CH_2CO$), 4.03 (q, $J_{HH}$ = 7.2 Hz, 2H, $CH_2$), 7.3–7.6 (m, 10H, Ph).

**[K(18-crown-6)][Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)OEt] (6).** Pure $Ph_2PCH_2C(O)OEt$ (3.68 g, 13.5 mmol) was added to a suspension of KH (0.56 g, 13.96 mmol) in THF (50 mL), and the reaction mixture was stirred for 0.5 h. The solution became light-orange and 18-crown-6 (3.57 g, 13.50 mmol) was added. After the reaction mixture was stirred for a few minutes, the solvent was removed and the red oil was treated with diethyl ether (50 mL). An orange microcrystalline solid was obtained which was filtered out and dried under vacuum (6.35 g, 82%). The product was purified by extraction with ether, and crystals suitable for X-ray diffraction were collected. Anal. Calcd for $C_{28}H_{40}KO_8P$ ($M$ = 574.69): C, 58.52; H, 7.02. Found: C, 58.47; H, 7.19. $^1$H NMR ($C_6D_6$): $\delta$ 1.46 (t, $J_{HH}$ = 7.0 Hz, 3H, $CH_3$), 3.17 (s, 24H, $OCH_2$), 3.82 (d, $J_{HP}$ = 7.5 Hz, 1H, =CH), 4.37 (q, $J_{HH}$ = 7.1 Hz, 2H, $CH_2$), 7.0–7.2 and 7.9 (m, 10H, Ph). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ −19.5 (s).

**Reaction of [K(18-crown-6)][Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)-Ph] (6) with $MeO_2C—C{\equiv}C—CO_2Me$ and Isolation of**

---

[30] Sakaki, S.; Aizawa, T.; Koga, N.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1989**, *28*, 103.

[31] (a) Issleib, K.; Thomas, G. *Chem. Ber.* **1960**, *93*, 803. (b) Braunstein, P.; Matt, D.; Mathey, F.; Thavard, D. *J. Chem. Res., Synop.* **1978**, 232; *J. Chem. Res., Miniprint* **1978**, 3041–3063.

**Table V. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 4 and 5**

| | 4 | 5 |
|---|---|---|
| chemical formula | $C_{32}H_{40}O_7PK$ | $C_{38}H_{52}N_2O_7PK\cdot 0.5C_4H_{10}O$ |
| *a* (Å) | 13.025(1) | 14.658(1) |
| *b* (Å) | 10.027(1) | 13.191(1) |
| *c* (Å) | 13.976(1) | 13.342(1) |
| α (deg) | 106.48(1) | 115.89(1) |
| β (deg) | 106.83(1) | 110.33(1) |
| γ (deg) | 97.98(1) | 65.25(1) |
| *V* (Å$^3$) | 1626.1(3) | 2064.4(3) |
| *Z* | 2 | 2 |
| fw | 606.7 | 756.0 |
| space group | $P\bar{1}$ (No. 1) | $P\bar{1}$ (No. 1) |
| *t* (°C) | 22 | 22 |
| λ (Å) | 1.541 78 | 0.710 69 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.239 | 1.216 |
| μ (cm$^{-1}$) | 22.61 | 2.10 |
| transm coeff | 0.959–1.000 | 0.855–1.000 |
| $R^a$ | 0.074 | 0.061 |
| $R_w{}^b$ | 0.091 | 0.065 |

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$.

**Table VI. Fractional Atomic Coordinates (×10$^4$) for Complex 4**

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| K | 2569(1) | −1178(1) | 2268(1) | C21 | 458(2) | 1964(3) | 3639(2) |
| P | 1922(1) | 1918(1) | 3825(1) | C22 | 117(2) | 3242(3) | 3841(2) |
| O1 | 2904(4) | −1530(4) | 300(3) | C23 | −1000(2) | 3212(3) | 3650(2) |
| O2 | 4712(3) | −1482(4) | 1973(4) | C24 | −1776(2) | 1903(3) | 3256(2) |
| O3 | 4273(3) | −1609(4) | 3835(3) | C25 | −1435(2) | 625(3) | 3053(2) |
| O4 | 2138(4) | −2890(4) | 3580(3) | C26 | −318(2) | 655(3) | 3245(2) |
| O5 | 392(3) | −2616(4) | 2021(4) | C31 | 2595(2) | 3316(3) | 5165(2) |
| O6 | 761(4) | −2500(5) | 169(4) | C32 | 3476(2) | 4438(3) | 5358(2) |
| O7 | 3488(3) | 1481(4) | 2557(3) | C33 | 4038(2) | 5397(3) | 6389(2) |
| C1 | 4001(7) | −1485(7) | 251(6) | C34 | 3719(2) | 5233(3) | 7228(2) |
| C2 | 4838(5) | −682(6) | 1362(7) | C35 | 2838(2) | 4111(3) | 7035(2) |
| C3 | 5469(4) | −792(7) | 3014(7) | C36 | 2276(2) | 3152(3) | 6004(2) |
| C4 | 5273(5) | −1695(7) | 3717(7) | C37 | 2191(3) | 2765(4) | 2931(3) |
| C5 | 4028(6) | −2458(7) | 4432(4) | C38 | 2908(3) | 2375(4) | 2419(3) |
| C6 | 2966(8) | −2335(8) | 4576(5) | C41 | 3064(2) | 3093(2) | 1623(2) |
| C7 | 1088(8) | −2824(8) | 3661(7) | C42 | 3351(2) | 2320(2) | 780(2) |
| C8 | 232(7) | −3501(8) | 2594(9) | C43 | 3548(2) | 2951(2) | 59(2) |
| C9 | −454(5) | −3095(13) | 1018(10) | C44 | 3457(2) | 4355(2) | 181(2) |
| C10 | −154(8) | −2178(12) | 341(9) | C45 | 3169(2) | 5128(2) | 1024(2) |
| C11 | 1072(9) | −1882(9) | −578(6) | C46 | 2973(2) | 4497(2) | 1744(2) |
| C12 | 2118(11) | −2134(10) | −638(6) | | | | |

**Table VII. Fractional Atomic Coordinates (×10$^4$) for Complex 5**

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| K | 5629(1) | 3581(1) | 2314(1) | C18 | 3549(6) | 2281(7) | 344(7) |
| P | 1106(1) | 2670(1) | −2474(1) | C21 | 464(3) | 4271(3) | −2280(3) |
| O1 | 5669(4) | 5837(4) | 4103(3) | C22 | 546(3) | 5086(3) | −1174(3) |
| O2 | 3856(3) | 5206(4) | 3149(4) | C23 | 80(3) | 6300(3) | −986(3) |
| O3 | 5748(4) | 1561(4) | 2697(4) | C24 | −468(3) | 6698(3) | −1904(3) |
| O4 | 7513(3) | 2125(4) | 3081(4) | C25 | −551(3) | 5883(3) | −3009(3) |
| O5 | 6309(3) | 3802(4) | 712(3) | C26 | −85(3) | 4669(3) | −3197(3) |
| O6 | 4759(3) | 2760(4) | −14(3) | C31 | −76(2) | 2301(3) | −2767(3) |
| N1 | 7484(4) | 4636(5) | 3094(4) | C32 | −778(2) | 3031(3) | −2052(3) |
| N2 | 3759(4) | 2836(5) | 1578(5) | C33 | −1615(2) | 2707(3) | −2180(3) |
| C1 | 4651(7) | 6679(6) | 4141(6) | C34 | −1749(2) | 1653(3) | −3022(3) |
| C2 | 3980(6) | 6147(7) | 4197(7) | C35 | −1047(2) | 923(3) | −3736(3) |
| C3 | 3129(6) | 4715(8) | 3105(7) | C36 | −211(2) | 1247(3) | −3609(3) |
| C4 | 2900(5) | 3884(8) | 1930(7) | O7 | 3218(3) | 1718(4) | −3117(3) |
| C5 | 3954(7) | 1986(9) | 2137(8) | C37 | 1423(4) | 2032(5) | −3821(5) |
| C6 | 4957(7) | 1051(7) | 2089(8) | C38 | 2446(4) | 1644(4) | −3927(5) |
| C7 | 6725(7) | 691(6) | 2595(7) | C41 | 2682(3) | 1054(3) | −5111(3) |
| C8 | 7522(5) | 1226(6) | 3407(6) | C42 | 1989(3) | 1342(3) | −6047(3) |
| C9 | 8273(5) | 2683(7) | 3837(6) | C43 | 2263(3) | 793(3) | −7109(3) |
| C10 | 8386(5) | 3381(8) | 3285(6) | C44 | 3228(3) | −45(3) | −7233(3) |
| C11 | 7403(6) | 5426(7) | 4161(5) | C45 | 3921(3) | −332(3) | −6297(3) |
| C12 | 6371(7) | 6331(6) | 4154(6) | C46 | 3647(3) | 217(3) | −5235(3) |
| C13 | 7521(5) | 4708(7) | 2192(6) | O1S | 85(35) | 393(25) | 221(26) |
| C14 | 7339(5) | 3817(7) | 1013(6) | C1S | −747(29) | −51(28) | 1008(28) |
| C15 | 6091(5) | 3029(6) | −406(5) | C2S | −665(33) | 187(45) | 199(37) |
| C16 | 4973(5) | 3148(6) | −719(5) | C3S | 240(24) | 246(27) | −929(27) |
| C17 | 3687(5) | 2876(6) | −286(5) | C4S | 1330(21) | 331(23) | −709(22) |

**[K(18-crown-6)][Ph$_2$P(O)O].** The alkyne (0.14 g, 1.00 mmol) was slowly added via a syringe to a solution of **6** (0.61 g, 1.01 mmol) in toluene (50 mL) at −78 °C. The solution was vigorously stirred and the temperature raised to 20 °C. A yellow solid was filtered out and dried (0.52 g).

**Reaction of 6 with PhC≡CPh.** A solution of **6** (0.53 g, 0.92 mmol) in toluene (30 mL) was added dropwise to a solution of diphenylacetylene (0.33 g, 1.84 mmol) in toluene (20 mL). The characteristic orange color of **6** turned instantly light-yellow. After stirring for 0.75 h, toluene was removed under reduced pressure and the yellow oil was treated with Et$_2$O (50 mL). The filtered solution was evaporated to dryness, and the white solid formed was treated with a mixture of hexane (50 mL) and Et$_2$O (20 mL). It was filtered out, dried, and collected (0.35 g, 51%). The $^1$H and $^{31}$P{$^1$H} NMR data were very similar to those of **6**. Another minor compound is also present: $^1$H NMR (C$_6$D$_6$) δ 1.38 (t, $J_{HH}$ = 7.0 Hz, 3H, CH$_3$), 3.20 (s, 24H, OCH$_2$), 4.36 (d, $J_{HP}$ = 24.5 Hz, 1H, =CH), 4.27 (q, $J_{HH}$ = 7.0 Hz, 2H, CH$_2$).

**Synthesis of [(8-mq)Pd{Ph$_2$PCH(AuPPh$_3$)C(O)Ph}]BF$_4$ (8).** AgBF$_4$ (0.096 g, 0.48 mmol) was added to a stirred solution of AuCl(PPh$_3$) (0.238 g 0.48 mmol) in THF (48mL). After 0.5 h the reaction mixture was filtered. (8-mq)Pd[Ph$_2$PCH$\cdots$C($\cdots$O)Ph] (0.265 g, 0.48 mmol) was added to the filtrate, and the reaction solution was stirred for 2 h, under the exclusion of light (like the following operations). The resulting solution was concentrated and filtered. A yellow solid was obtained and recrystallized from CH$_2$Cl$_2$/hexane, affording white crystals of the product (0.124 g, 22%). Anal. Calcd for C$_{48}$H$_{39}$BAuF$_4$NP$_2$OPd (*M* = 1097.99): C, 52.51; H, 3.58; N, 1.28. Found: C, 51.68; H, 3.42; N, 1.30. IR (KBr): 1514 (m), 1504 (s), 1481 (m), 1437 (s) cm$^{-1}$; ν(BF$_4$) 1102 (s), 1083 (s), 1056 (vs), 1024 (m) cm$^{-1}$. IR of the $^1$H NMR sample in CD$_2$Cl$_2$: 1506 (s), 1438 (m) cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 3.67 (d, 2H, CH$_2$, $^3J$(PH) = 2.7 Hz), 5.26 (t, 1H, PCH, $^2J$(P$_{Pd}$H) = $^3J$(P$_{Au}$H) = 8.4 Hz), 7.06–9.23 (36H, aromatic H). $^{31}$P{$^1$H} NMR (C$_6$D$_6$/CH$_2$Cl$_2$): (AB spin system) δ$_A$ 33.0 (1P, P(Pd)) δ$_B$ 39.2 (1P, P(Au)), $^3J$(AB) = 11.6 Hz. MS: *m/e* 1010 (M$^+$).

**X-ray Crystallography.** The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with the structure refinement are given in Table V. The reduced cells were obtained with the use of TRACER.[32] Data were collected at room temperature on a single-crystal four circle diffractometer. For intensities and background individual reflection profiles were analyzed.[33] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[34] and the absolute scale was established by the Wilson method.[35] The crystal quality was tested by Ψ scans showing that crystal absorption effects could not be neglected for complex **4**. The related intensity data were then corrected for absorption using

---

(32) Lawton, S. L.; Jacobson, R. A. TRACER, a cell reduction program. Ames Laboratory, Iowa State University of Science and Technology, 1965.

(33) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580.

(34) Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using: Sheldrick, G. *SHELX-76. System of Crystallographic Computer Programs*; University of Cambridge: Cambridge, England, 1976.

(35) Wilson, A. J. C. *Nature* **1942**, *150*, 151.

ABSORB.[36] The function minimized during the full matrix least-squares refinement was $\Sigma w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. Scattering factors for neutral atoms were taken from ref 37a for non-hydrogen atoms and from ref 38 for H. Anomalous scattering corrections were included in all structure factor calculations.[37b] Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by direct methods using SHELX86.[39] Refinement was first isotropically, and then anisotropically for all the non-hydrogen atoms except for the $Et_2O$ solvent molecule (complex **5**) which was found to be statistically distributed around a center of symmetry. All the hydrogen atoms, but those associated with the $Et_2O$ molecule, which were ignored, either located from a $\Delta F$ map or put in geometrically calculated positions were introduced as fixed contributors prior to the last stage of refinement ($U_{iso}$ = 0.12 and 0.08 Å$^2$ for complexes **4** and **5**, respectively). Selected bond distances and angles are quoted in Tables I and II, and final atomic coordinates are listed in Tables VI and VII for non-H atoms for complexes **4** and **5**, respectively.[40]

**Acknowledgment.** We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-33420-92) and the CNRS for financial support and the Université Louis Pasteur for a Visiting Professorship to C.F. The calculations have been carried out at the Centre de Calcul de Strasbourg-Cronenbourg. We thank the staff of the Centre for their cooperation.

**Supplementary Material Available:** Tables of experimental details associated with data collection (Table SI), unrefined hydrogen coordinates (Tables SII, SIII), thermal parameters (Tables SIV, SV), and bond distances and angles (Tables SVI, SVII) for complexes **4** and **5** (10 pages). Ordering information is given on any current masthead page.

OM9302103

---

(36) Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

(37) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, (a) p 9, (b) p 149.

(38) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(39) Sheldrick, G. *SHELX-86. A FORTRAN-77 program for the solution of crystal structure from diffraction data*; University of Cambridge: Cambridge, England, 1986.

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

(41) Note Added in Proof. This structure has now been confirmed by an X-ray diffraction study: Braunstein, P.; Ingold, F.; Tiripicchio, A., unpublished results.