Hybrid Ligands. A New Route to (Carbamoylmethyl)phosphines. Molecular Structure of [(*o*-$C_6H_4CH_2NMe_2$)Pd{Ph_2PC=C(O)N(Ph)N=C(Me)}]

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The (carbamoylmethyl)phosphines $Ph_2PCH_2C(O)NRR'$ (R = R' = Ph (**4**); R = Me, R' = Ph (**5**), R = R' = Me (**6**)) were obtained in high yields by reaction of chlorodiphenylphosphine with the enolates obtained from the corresponding acetamides, Li[$CH_2C(O)NRR'$]. This methodology was extended to the synthesis of the sodium phosphinopyrazolonate [Ph_2PC=C(O)N(Ph)N=C(Me)]Na (**9**). Treatment of **9** with sulfur yields the phosphine sulfide [$Ph_2P(S)C$=C(O)N(Ph)N=C(Me)]Na (**10**). Compound **9** reacts with [(*o*-$C_6H_4CH_2NMe_2$)PdCl]$_2$ and $Pd(acac)_2$ to yield respectively the chelate complexes [(*o*-$C_6H_4CH_2NMe_2$)Pd{Ph_2PC=C(O)N(Ph)N=C(Me)}] (**11**) and *cis*-[Pd{Ph_2PC=C(O)N(Ph)N=C(Me)}$_2$] (**12**). The molecular structure of complex **12** was determined crystallographically: space group $P2/c$, a = 10.863(4) Å, b = 12.575(4) Å, c = 14.562(6) Å, β = 103.43(3)°, V = 1935(1) Å^3, and Z = 2. The palladium atom, which lies on a C_2 axis, is complexed by two anionic chelating *cis*-*P*,*O* ligands (Pd–P = 2.248(1) Å; Pd–O = 2.078(3) Å). The aromatic pyrazole system is planar; the dihedral angle between this plane and the metal plane is 1.4(8)°, and that with the N-bonded phenyl ring is 7.7(8)°. All compounds were characterized by elemental analysis and IR and ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy.

Introduction

Since the early 70's, phosphines with functional group substituents have increasingly attracted the attention of a number of chemists,[2] and many studies have been centered on their use as ligands in transition metal chemistry.[3] It has often been shown that in complexes based on such ligands the functional group(s) may be helpful for finely controlling or enhancing the reactivity of the metal center and/or facilitating the catalytic or stoichiometric transformation of a substrate within the coordination sphere. This latter point is generally achieved through specific interactions between the substrate and the functional group.[4] Other phosphines in which the functional group does not participate directly in metal or substrate binding, but may exert a long-range influence on the metal via the phosphorus atom, are sometimes suitable for the control of the physical properties, *e.g.* magnetism, of metal complexes.[5] The aim of this report is to present a new synthetic route to (carbamoylmethyl)phosphines, $R_2PCH_2C(O)NR'_2$, a class of hybrid ligands which has only scarcely been studied.[6] As can be deduced from extensive studies of the corresponding phosphine oxides, largely investigated because of their ability to extract actinides from nuclear waste, the carbamoyl group presents high stability in neutral and acidic media.[7] An adequate choice of the R' groups may allow the tuning of the coordinating ability of the carbonyl group as well as the control of the solubility of the complexes that will contain such ligands. As an extension of this study, we also describe the synthesis of the sodium phosphinopyrazolonate [Ph_2PC=C(O)N(Ph)N=C(Me)]Na (**9**), which allows the preparation of new *P*,*O* chelate complexes. A part of this work has been published as a preliminary account.[8]

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry argon by using Schlenk-tube techniques. Solvents were dried over suitable reagents and freshly distilled under argon before use. IR spectra were recorded on a IFS Bruker spectrometer. A Bruker WP 200 SY instrument was used to obtain the ^{1}H, ^{13}C, and ^{31}P NMR spectra. ^{1}H and ^{13}C data were referenced to external $(CH_3)_4Si$, and ^{31}P NMR data, to external 85% H_3PO_4. The mass spectra were recorded on a Finnigan MAT TSQ-70 spectrometer or a ZAB HF analytical instrument (FAB spectra). The amides used here were prepared by acetylation of the

(1) (a) EHICS. (b) University of Rennes.
(2) A major contribution in this field was the discovery of the spectacular properties of the DIPAMP ligand. See for example: Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Homogeneous Catalysis*; Advances in Chemistry Series 132; American Chemical Society: Washington, DC, 1974; Vol. II, pp 274–282.
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corresponding primary amine.[9] The complexes $[Pd(acac)_2]$[10] and $[\{(o\text{-}C_6H_4CH_2NMe_2)Pd(\mu\text{-}Cl)\}_2]$[11] were synthesized by published procedures.

Preparation of $Ph_2PCH_2C(O)NPh_2$ (4). A 1.6 M hexane solution of *n*-BuLi (17.8 mL, 28.4 mmol) was dropwise added to a solution of diisopropylamine (2.874 g, 28.4 mmol) in THF (100 mL) at −78 °C. After the mixture had been stirred for 2 h, a solution of *N,N*-diphenylacetamide (6.023 g, 28.4 mmol) in THF (50 mL) was added slowly within 5 min. The mixture was stirred for 2 h at −78 °C and then transferred into a Schlenk flask containing Ph_2PCl (6.266 g, 28.4 mmol) in THF (50 mL). After the mixture was stirred for 15 h at room temperature, the solvent was removed in vacuo. The residue was treated with hot toluene (100 mL), and the resulting suspension was filtered through a glass frit. The pale yellow filtrate was then concentrated and precipitated with pentane. The white precipitate thus obtained was recrystallized from ethanol (colorless crystals, 10.440 g, 26.40 mmol, 93%). Mp: 132–133 °C. ^1H NMR ($CDCl_3$): δ 7.45–7.14 (20 H, aromatic H), 3.20 (s, 2H, PCH_2, $^2J(PH)$=0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.90 (d, CO, $^2J(PC)$ = 9 Hz), 142.72–126.35 (aromatic C), 36.39 (d, PCH_2, $J(PC)$ = 20 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.5 (s). IR (KBr): 1658 s (ν(C=O)) cm^{-1}. Anal. Calcd for $C_{26}H_{22}NOP$ (M_r = 395.44): C, 78.97; H, 5.61; N, 3.54. Found: C, 78.90; H, 5.48; N, 3.42.

Preparation of $Ph_2PCH_2C(O)NMePh$ (5). A 1.6 M hexane solution of *n*-BuLi (12.5 mL, 20.0 mmol) was added slowly to a solution of hexamethyldisilazane (3.308 g, 20.5 mmol) in THF (100 mL) at −78 °C. After the mixture had been stirred for 0.5 h, a solution of dry *N*-methylacetanilide (2.984 g, 20.0 mmol) in THF (100 mL) was added slowly. The mixture was stirred for 1 h at −78 °C and then transferred into a Schlenk flask containing Ph_2PCl (4.413 g, 20.0 mmol) in THF (30 mL). After the mixture was stirred for 15 h at room temperature, the solvent was removed in vacuo. The residue was treated with toluene, and the resulting suspension was filtered through a glass frit. The yellow filtrate was then evaporated to dryness yielding a white sometimes yellowish residue which was chromatographed on a column (Silicagel 60, 230–400 mesh ASTM) using a mixture of AcOEt (20% volume)–hexane as eluant (R_f=0.15). This gave a colorless oil which crystallizes slowly (4.670 g, 14.0 mmol, 70%). Mp: 50–51 °C. ^1H NMR ($CDCl_3$): δ 7.35–7.06 (15 H, aromatic H), 3.93 (s, 3H, NMe), 2.97 (s, 2H, PCH_2, $^2J(PH)$=0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −14.7 (s). IR (neat): 1645 s (ν(C=O)) cm^{-1}. MS (EI): *m/e* 333 (M^+, 34%). Anal. Calcd for $C_{21}H_{20}NOP$ (M_r = 333.37): C, 75.66; H, 6.05; N, 4.20. Found: C, 75.67; H, 6.26; N, 4.25.

Preparation of $Ph_2PCH_2C(O)NMe_2$ (6). This compound was prepared using a procedure similar to that described above for **4** (yield 90%, white product). The product was recrystallized from cold EtOH. Mp: 97–98 °C. ^1H NMR ($CDCl_3$): δ 7.51–7.26 (10 H, aromatic H), 3.17 (s, 2H, PCH_2, $^2J(PH)$=0 Hz), 2.95 (s, 3H, NMe), 2.89 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −18.4 (s). IR (KBr): 1632 s (ν(C=O)) cm^{-1}. Anal. Calcd for $C_{16}H_{18}NOP$ (M_r = 271.18): C, 70.84; H, 6.64; N, 5.16. Found: C, 71.28; H, 6.79; N, 5.04.

Preparation of $Ph_2P(O)CH_2C(O)NMePh$ (7). A solution of H_2O_2 in water (10 mL, concentration 30%) was added with stirring to $Ph_2PCH_2C(O)NMePh$ (3.334 g, 10.00 mmol) in CH_2Cl_2 (50 mL). After 12 h, the mixture was treated with sodium bisulfite. The layers were separated, and the dichloromethane solution was dried over magnesium sulfate. The product was chromatographed (Silicagel 60) using a mixture of MeOH (10% volume)–CH_2Cl_2 as eluant (R_f=0.65). The product was obtained as a colorless oil which crystallizes quickly (3.142 g, 9.0 mmol, 90%). Mp: 131–145 °C. ^1H NMR ($CDCl_3$): δ 7.81–6.99 (15 H, aromatic H), 3.37 (d, 2H, PCH_2, $^2J(PH)$=15.5 Hz), 3.17 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.3 (s). IR (KBr): 1654 s (ν(C=O)), 1192 s (ν(P=O)) cm^{-1}. Anal. Calcd for $C_{21}H_{20}NO_2P$ (M_r = 349.12): C, 72.20; H, 5.77; N, 4.01. Found: C, 72.33; H, 5.75; N, 3.98.

Preparation of $Ph_2P(S)CH_2C(O)NPh_2$ (8). Sulfur (0.320 g, 10.00 mmol) was added to a solution of $Ph_2PCH_2C(O)NPh_2$ (3.950 g, 10.00 mmol) in toluene. The mixture was heated at 60 °C for 2 min, and a white precipitate appeared. The product was filtered off and dried in vacuo (3.500 g, 8.19 mmol, 82%). Mp: 197–198 °C. ^1H NMR ($CDCl_3$): δ 7.95–7.11 (20 H, aromatic H), 3.74 (d, 2H, PCH_2, $^2J(PH)$=14 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.0 (s). IR (KBr): 1665 s (ν(C=O)) cm^{-1}. Anal. Calcd for $C_{26}H_{22}NOPS$ (M_r = 427.51): C, 73.05; H, 5.19; N, 3.28; S, 7.50. Found: C, 73.1; H, 5.3; N, 4.0; S, 7.4.

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Preparation of $[Ph_2PC(=C(O)N(Ph)N=C(Me)]Na$ (9). A solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (3.600 g, 20.67 mmol) in THF (150 mL) was stirred at 0 °C for 20 min in the presence of NaH (1.000 g, 41.70 mmol). After addition of Ph_2PCl (4.556 g, 20.67 mmol), the mixture was refluxed for 3 h. Then the solution was evaporated to dryness. The residue was treated with CH_2Cl_2 (300 mL) and the resulting suspension filtered through a glass fritt. After concentration of the filtered solution, pentane was added to afford **9** as white microcrystals (5.880 g, 80%). The product slowly decomposes at $T > 190$ °C. ^1H NMR ($CDCl_3$): δ 6.83–7.20 (15 H, aromatic H), 1.67 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 168.58 (d, CO, $^2J(PC)$=39.5 Hz), 152.51 (d, C=N, $^2J(PC) \approx 12$ Hz), 140.58–121.50 (aromatic C), 84.82 (d, PC, $^1J(PC) \approx 22$ Hz), 15.82 (s, Me). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ −34.5 (s). IR ($CHCl_3$): 1601 s, 1591 sh, 1547 s br, 1505 s. IR (KBr): 1449 s (pyrazole), 1585 s br (pyrazole), 1599 sh, 1600 s (pyrazole), 3192 s br, 3335 s br cm^{-1}. MS (EI): *m/e* 358 (M − Na + H^+, 18%). The FAB MS spectrum shows an intense peak (100%) at *m/e* 397.1 (M + O + H^+) as well as other peaks at *m/e* 419.1 (28%, M + 2O + H^+) and *m/e* 793.2 (6%, 2M + 4O + H^+) suggesting an oligomeric structure for the salt. Anal. Calcd for $C_{22}H_{18}NaN_2OP{\cdot}0.5CH_2Cl_2$ (M_r = 380.11 + 42.47): C, 63.91; H, 4.53. Found: C, 64.46; H, 5.18.

Preparation of $[Ph_2P(S)C(=C(O)N(Ph)N=C(Me)]Na$ (10). Sulfur (0.110 g, 3.43 mmol) was added to a solution of $[Ph_2PCC(O)N(Ph)N=C(Me)]Na$ (1.274 g, 3.35 mmol) in CH_2Cl_2 (50 mL). A white precipitate appeared after 10 min, which was filtered off and dried in vacuo (1.100 g, 84%). This product slowly decomposes at $T >$ 200 °C. ^1H NMR ($CDCl_3$): δ 7.76–7.03 (15 H, aromatic H), 1.65 (s, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.6 (s). IR (KBr): 1600 s, 1599 sh, 1586 s br, 1501 s, 1482 ms, 1454 s, 1435 s cm^{-1}. MS (EI): *m/e* 390 (M − Na + H^+, 100%). Anal. Calcd for $C_{22}H_{18}NaN_2OPS$ (M_r = 412.43): C, 64.07; H, 4.40; N, 6.79; S, 7.78. Found: C, 64.25; H, 4.79; N, 6.55; S, 7.6.

Preparation of $[Ph_2P(S)C(=C(OH)N(Ph)N=C(Me)]$ (10′). An aqueous solution (50 mL) of $[Ph_2P(S)C(=C(O)N(Ph)N=C(Me)]Na$ (0.412 g, 1.00 mmol) was reacted with 1 mL of concentrated HCl. The white precipitate formed was filtered out, washed with Et_2O, and dried under vacuo (0.360 g, 92%). ^1H NMR ($CDCl_3$): δ 1.74 (s, 3H, Me), 7.18–7.80 (15H, aromatic H), 11.26 (OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.4 (s) ppm. Anal. Calcd for $C_{22}H_{19}N_2OPS$ (M_r = 390.45): C, 67.68; H, 4.91; N, 7.17. Found: C, 65.94; H, 4.90; N, 7.48.

Preparation of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCC(O)N(Ph)N=C(Me)\}]$ (11). A mixture of $[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$ (0.222 g, 0.40 mmol) and $[Ph_2PC(=C(O)N(Ph)N=C(Me)]Na$ (0.304 g, 0.80 mmol) was stirred for 12 h in THF (20 mL). The mixture was filtered and concentrated, and pentane was added affording a yellow powder. The product was recrystallized from toluene–pentane (yellow crystals, 0.216 g, 87%). ^1H NMR ($CDCl_3$): δ 8.08–6.72 (19H, aromatic H), 3.96 (d, 2H, NCH_2, $^4J(PH)$=1.7 Hz), 2.90 (d, 6H, NMe_2, $^4J(PH)$=2.3 Hz), 1.89 (s, 3H, Me of pyrazolonate ring). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 7.0 (s). IR (KBr): 1596 m, 1585 ms, 1530 s, 1502 s. Anal. Calcd for $C_{31}H_{30}N_3OPPd{\cdot}0.25$ toluene (M_r = 621.01): C, 63.54; H, 5.27; N, 6.51. Found: C, 63.34; H, 5.19; N, 6.76.

Preparation of *cis*-$[Pd\{Ph_2PC(=C(O)N(Ph)N=C(Me)\}_2]$ (12). A solution of $[Ph_2PC(=C(O)N(Ph)N=C(Me)]Na$ (0.717 g, 2.00 mmol) in CH_2Cl_2 (50 mL) was added to a suspension of $Pd(acac)_2$ (0.548 g, 1.80 mmol) in CH_2Cl_2 (20 mL). The mixture immediately turned red and was filtered and concentrated, and pentane was added affording a powder, which was recrystallized from THF–pentane. Crystals suitable for X-ray diffraction were obtained from THF–benzene/pentane (red-orange crystals, 1.330 g, 90%). Mp: >220 °C. The product darkens progressively on heating above 200 °C. ^1H NMR ($CDCl_3$): δ 8.00–7.06 (30H, aromatic H), 1.66 (s, 6H, Me). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 6.7 (s). IR (KBr): 1594 m, 1580 sh, 1523 s, 1501 s. Anal. Calcd for $C_{44}H_{36}N_4O_2P_2Pd$ (M_r = 821.15): C, 64.36; H, 4.42; N, 6.82. Found: C, 64.22; H, 4.49; N, 6.71.

X-ray Data Collection and Structure Solution and Refinement for 12. Crystallographic data for **12** are collected in Table I. Red-orange crystals suitable for diffraction were obtained by slow diffusion of pentane into a THF–benzene (1:9) solution of the complex. The unit cell was obtained from the angular settings of 25 reflections ($20° \le 2\theta \le 27°$). Intensity data were collected on an automatic four-circle diffractometer. No decay

Table I. Crystal data for **12**

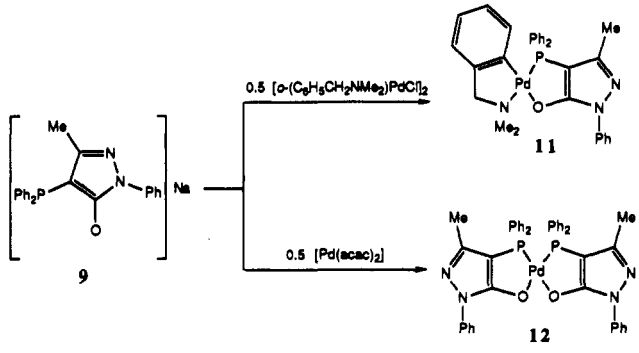
formula: $C_{44}H_{36}N_4O_2P_2Pd$	fw = 821.15
cryst system: monoclinic	space group: $P2/c$ (No. 13)
a = 10.863(4) Å	λ = 0.710 73 Å (Mo Kα)
b = 12.575(4) Å	ρ_{calcd} = 1.409 g cm^{-3}
c = 14.562(6) Å	μ(Mo Kα) = 5.944 cm^{-1}
β = 103.43(3)°	R^a = 0.036
V = 1935(1) Å^3	$R_w{}^b$ = 0.049
Z = 2	
T = 294 ± 2 K	

$^a R = \sum||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Atomic Coordinates with Isotropic Thermal Parameters (B's) for **12**

atom	x	y	z	B (Å^2)
Pd	1.000	0.02442(4)	0.250	2.638(9)
P	0.8394(1)	−0.0920(1)	0.21065(8)	2.74(3)
O	0.8662(3)	0.1451(3)	0.2185(2)	3.10(7)
N(1)	0.6441(4)	0.1652(3)	0.1637(3)	3.36(9)
N(2)	0.5380(4)	0.0993(4)	0.1356(3)	4.0(1)
C(1)	0.7527(4)	0.1062(4)	0.1892(3)	2.9(1)
C(2)	0.7168(4)	0.0009(4)	0.1776(3)	3.2(1)
C(3)	0.5824(4)	0.0021(4)	0.1434(4)	3.6(1)
C(4)	0.4941(5)	−0.0898(5)	0.1175(5)	5.2(2)
C(5)	0.6295(5)	0.2774(4)	0.1583(4)	3.5(1)
C(6)	0.5103(5)	0.3167(5)	0.1177(5)	5.3(2)
C(7)	0.4954(6)	0.4257(5)	0.1087(6)	7.2(2)
C(8)	0.5923(7)	0.4933(5)	0.1397(6)	7.1(2)
C(9)	0.7105(6)	0.4536(5)	0.1807(5)	5.4(2)
C(10)	0.7291(5)	0.3448(4)	0.1905(4)	4.1(1)
C(11)	0.8093(4)	−0.1754(4)	0.3049(3)	3.0(1)
C(12)	0.8554(5)	−0.1433(5)	0.3986(4)	4.0(1)
C(13)	0.8285(6)	−0.2035(5)	0.4707(4)	5.3(1)
C(14)	0.7544(7)	−0.2932(5)	0.4501(4)	6.6(2)
C(15)	0.7089(6)	−0.3244(5)	0.3590(4)	5.6(1)
C(16)	0.7341(5)	−0.2648(5)	0.2863(4)	4.5(1)
C(17)	0.8380(5)	−0.1789(4)	0.1117(4)	3.5(1)
C(18)	0.8858(5)	−0.2818(4)	0.1222(4)	4.3(1)
C(19)	0.8920(6)	−0.3418(5)	0.0431(5)	5.8(2)
C(20)	0.8526(7)	−0.2990(6)	−0.0454(4)	7.2(2)
C(21)	0.8056(7)	−0.1972(6)	−0.0562(4)	6.6(2)
C(22)	0.7988(5)	−0.1362(5)	0.0204(4)	4.7(1)

Scheme I



was observed during the data collection period. For all subsequent computations the Enraf-Nonius package was used.[12] Intensities were corrected for Lorentz-polarization factors. Absorption corrections were omitted in view of the low absorption coefficient. The crystal structure was solved by using the MULTAN program 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 $w = 4I/\sigma^2(I) + (0.06I)^2$. Hydrogen atoms were introduced at their computed coordinates (C–H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of B=5 Å^2. The final difference map showed no significant residual peaks. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for

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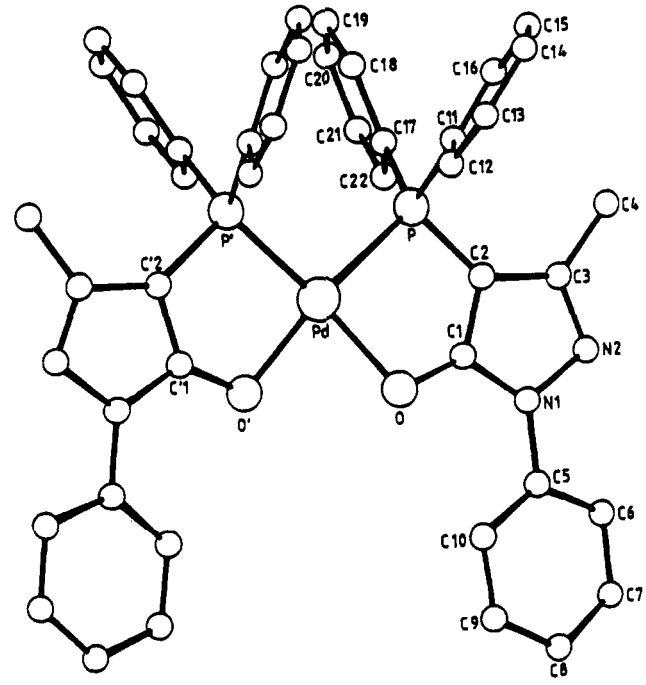

Figure 1. Molecular structure and atom-labeling scheme for **12**.

Table III. Selected Bond Distances and Angles for **12**

	Distances (Å)		
Pd–P	2.248(1)	C(2)–C(1)	1.379(6)
Pd–O	2.078(3)	C(2)–C(3)	1.429(6)
P–C2	1.753(4)	C(3)–C(4)	1.494(7)
P–C11	1.817(4)	C(3)–N(2)	1.308(6)
P–C17	1.806(5)	N(1)–N(2)	1.401(5)
C1–O	1.303(5)	C(1)–N(1)	1.370(5)
	Angles (deg)		
P–Pd–O	87.58(8)	O'–Pd–O	86.15(8)
Pd–P–C2	97.5(1)	P–Pd–O'	173.78(9)
Pd–P–C17	117.4(2)	N1–N2–C3	105.4(4)
Pd–P–C11	116.7(1)	C1–C2–C3	105.6(4)
P–C2–C1	115.6(3)	C2–C1–O	128.3(4)
P'–Pd–P	98.69(8)	C1–N1–C5	129.1(4)
		N2–N1–C5	119.9(4)

all non-hydrogen atoms were obtained from standard sources.[13] Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table II. Further tables are available as supplementary material (see paragraph at end of paper regarding supplementary material).

Results and Discussion

The direct C-phosphination at the methyl carbon of carbonyl compounds of the type $CH_3C(O)R$ *via* the derived enolates has first been described in 1964.[14] Although this reaction opens interesting synthetic perspectives with respect to the preparation of various organophosphorus compounds and in particular of carbonyl-activated phosphorus(V) compounds, this methodology has only been applied to some ketone and ester enolates.[15] Indeed these latter anions react selectively at the C-atom with chlorophosphines or chlorophosphites. Whether this strategy may be

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(14) Ponomarev, S. V.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1964**, *34*, 3450.

(15) (a) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765–3770. (b) Douce, L.; Matt, D. *C. R. Acad. Sci. Paris* **1990**, *310 II*, 721–726. (c) Knight, D. A.; Cole-Hamilton, D. J.; Cupertino, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 3051–3054. (d) Matt, D.; Van Dorsselaer, A. *Polyhedron* **1991**, *10*, 1521–1526. (e) Perera, S. D.; Shaw, B. L. *J. Organomet. Chem.* **1991**, *402*, 133–138. (f) Boeckman, R. K., Jr.; Kamenecka, T. M.; Nelson, S. G.; Pruitt, J. R.; Barta, T. E. *Tetrahedron Lett.* **1991**, *32*, 2581–2584.

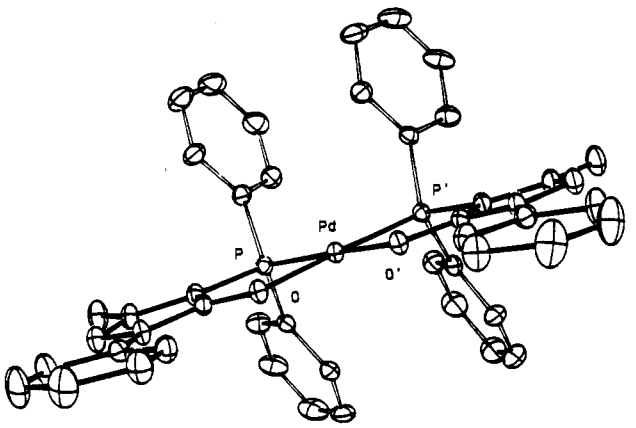
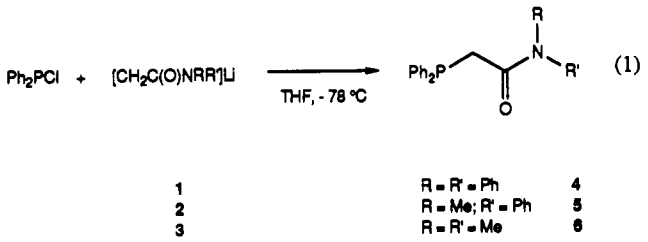


Figure 2. Perspective view of **12**.

applied to other carbonyl compounds containing at least one acidic hydrogen in the α position to the carbonyl group still remains questionable; the results given below will concern our investigations on acetamides.

The lithium enolates $Li[CH_2C(O)N(R)(R')]$ (R = R' = Ph (**1**); R = Me, R' = Ph (**2**); R = R' = Me (**3**)), obtained by reaction of the corresponding acetamides with $LiN(SiMe_3)_2$ or $LiN(i\text{-}C_3H_7)_2$, react with chlorodiphenylphosphine to quantitatively yield the phosphines **4**–**6**, respectively (eq 1). The

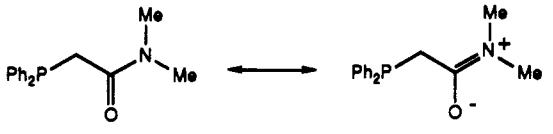


(1)

1	R = R' = Ph	4
2	R = Me; R' = Ph	5
3	R = R' = Me	6

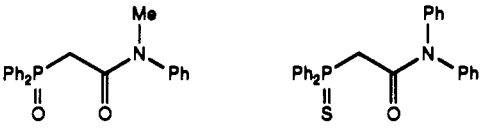
phosphorus NMR signals of these compounds ($\delta(CDCl_3)$ −13.5 ppm for **4**, −14.7 ppm for **5**, −18.9 ppm for **6**) appear in the range expected for methyldiphenylphosphine-derived compounds of the type Ph_2PCH_2X[16] (for comparison the signal of Ph_2PMe appears at −28 ppm).

It is noteworthy that in the ^1H NMR spectrum of *each* compound, the PCH_2 protons appear as a singlet ($\delta(PCH_2)$=3.20 for **4**, 2.97 ppm for **5**, 3.17 ppm for **6**). A $^2J(PCH_2)$ coupling constant close to zero is a general observation for phosphines of the type $Ph_2PCH_2C(O)R$.[15b,d,17] As expected for amides of general formula $R_2NC(O)CH_3$,[18] the *N*-methyl groups of phosphine **6** appear as two distinct signals in the room-temperature ^1H NMR spectrum (200 MHz). This nonequivalence corresponds to the syn/anti spatial arrangement of the methyl groups with respect to the carbonyl group and is due to the restricted rotation about the C–N bond.



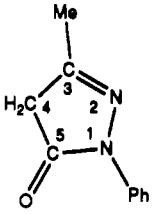
A similar limited degree of rotation about the C–N bond is likely to occur for the two other phosphines reported here. Note that the X-ray analysis of **5**, published previously,[8] confirms the partial double-bond character of the N–C(O) bond (1.34 Å) in such ligands.

Treatment of **5** with an aqueous H_2O_2 solution (30%) quantitatively led to the corresponding phosphine oxide **7**. On



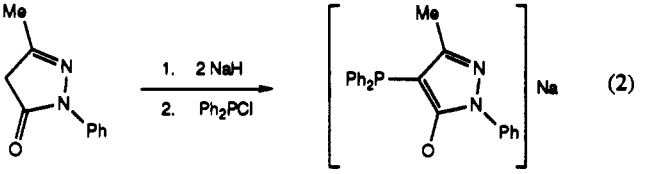
7 **8**

heating of a toluene solution of compound **4** in the presence of 1 equiv of S_8, the phosphine sulfide **8** precipitated in high yield within a few minutes (for the characterization of **7** and **8**, see Experimental Section). In an attempt to extend the synthetic methodology described above, we aimed at branching a diphenylphosphino group on the C4 atom of 3-methyl-1-phenyl-2-pyrazolin-5-one, **AH**. This pyrazolone contains an acidic proton



AH

in an α position to the ketone function and has previously been shown to undergo functionalizations on the corresponding C4 atom.[19] Treatment of **AH** with *2 equiv* of sodium hydride in THF (0 °C) and subsequent reaction with 1 equiv of Ph_2PCl (reflux, 3 h) afforded the salt **9** quantitatively, as verified by ^{31}P NMR spectroscopy (eq 2).



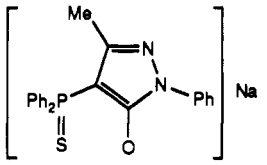
(2)

9

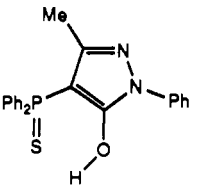
The coupling reaction occurs selectively at the C4 atom. The phosphorus-substituted carbon atom is characterized by a doublet at 84.82 ppm ($^1J_{PC}$=22 Hz) in the ^{13}C NMR spectrum (*vs* 43.06 ppm for the C4 carbon atom in **AH**), and the C–O signal appears at 168.58 ppm (*vs* 170.6 ppm for the C=O carbon atom in **AH**). The FAB MS spectrum confirms the presence of sodium (see Experimental Section). Compound **9** is also formed when a 1:1 pyrazolone–base ratio is used instead of 1:2; in this case, however, the yield was only *ca.* 50% and another unidentified product was detected by NMR (^{31}P signal at −33 ppm). The latter could possibly correspond to the protonated form $Ph_2PC{=}C(OH)N{-}(Ph)N{=}C(Me)$ (**9'**). Since acidolysis or simple hydrolysis of the reaction mixture led to unidentified decomposition products, the phosphine **9'** was isolated as its salt, **9**, with *ca.* 80% yield using the procedure described above with 2 equiv of sodium hydride

(16) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J., Quin, D. L., Eds.; VCH Publishers: Deerfield Beach, FL; pp 1–60.
(17) Kakli, M. A.; Gray, G. M.; Delmar, E. G.; Taylor, R. C. *Syn. React. Inorg. Metal-Org. Chem.* **1975**, *5*, 357–371.
(18) Günther, H. *NMR Spectroscopy*, 3rd ed.; Thieme Verlag: Stuttgart, Germany, 1992; p 303.
(19) (a) Jensen, B. S. *Acta Chem. Scand.* **1959**, *13*, 1668–1670. (b) Wilke, G.; Bechmann, W.; Uhlemann, E. *Z. Anorg. Allg. Chem.* **1977**, *428*, 277. (c) Uhlemann, E.; Maack, B.; Raab, M. *Anal. Chim. Acta* **1980**, *116*, 153–160. (d) Morinaka, Y.; Nishi, H.; Watanabe, T.; Yuki, T.; Sakurai, Y. Jpn. Kokai Tokkio Koho JP 62149617, Jul 3, 1987, Appl. 85/290687, Dec 25, 1985; *Chem. Abstr.* **1985**, *108*, 11247k. (e) Todorova, O.; Ivanova, E.; Terebenina, A.; Jordanov, N.; Dimitrova, K.; Borisov, G. *Talanta* **1989**, *8*, 817–820.

and without performing hydrolysis during the workup. By comparison with those of **4–6**, the ^{31}P NMR spectrum of **9** displays a highfield-shifted signal (−34.5 ppm), consistent with the strong electron-withdrawing effect of the pyrazole moiety.[20] When **9** was treated with S_8 in CH_2Cl_2, the phosphine sulfide **10** was



10



10'

quantitatively formed (for its characterization, see Experimental Section). This salt is water soluble. On adding of HCl to an aqueous solution of **10**, the phosphine sulfide **10'** precipitated. This compound is characterized by an OH signal at 11.26 ppm in the ^1H NMR spectrum and a signal at 29.4 ppm in the ^{31}P NMR spectrum.

Treatment of a THF solution of the palladium dimer $[(o\text{-}C_6H_4CH_2NMe_2)PdCl)]_2$ with 2 equiv of **9** quantitatively yielded complex **11** (Scheme I). As deduced from the values of the $^4J(PNCH_3)$ and $^4J(PNCH_2)$ coupling constants (2.3 and 1.7 Hz, respectively), the phosphorus and the nitrogen atoms occupy trans positions. The IR spectrum of this complex shows the typical[21] absorption bands of the pyrazolonato moiety in the region 1600–1400 cm^{-1} (see Experimental Section).

A bis(pyrazolonato–phosphine) complex was instantly generated by reaction of $Pd(acac)_2$ with 2 equiv of **9** in THF (Scheme I). The thus formed complex **12** was characterized by IR and ^{31}P and ^1H NMR spectroscopy (see Experimental Section). Since these data led to no conclusion about the *cis* or *trans* stereochemistry of the complex, an X-ray diffraction study was undertaken.

The molecular structure of complex **12** is represented in Figure 1 together with the atomic numbering scheme. Selected bond distances and angles are given in Table III. The molecule has C_2 symmetry. This study establishes that the phosphorus atoms occupy cis positions and that the palladium center is complexed by two anionic P,O ligands. The bite angle of these chelating ligands is 87.58°. The P–Pd–P′ angle of 98.69(8)° contrasts with the O–Pd–O′ angle (86.15(9)°) and reflects some degree of repulsion between the PPh_2 groups. The Pd–P bond distances (2.248(1) Å) and the Pd–O bond distances (2.078 Å) fall in the expected ranges.[22] The P–C(2) bond length is significantly shorter than the P–C(11) and P–C(17) distances, suggesting some electron delocalization in the metallocycles. The pyrazole moiety is planar within experimental error, and the bond lengths in the ring are consistent with its aromaticity. The C(5)–C(10) phenyl ring is only slightly inclined to the pyrazole plane (7.7°), thus showing the high degree of conjugation between these two rings. The coordination plane displays an angle of 1.4(8)° with the pyrazole ring; the high planarity of the chelating systems is illustrated in Figure 2.

In conclusion, the reaction of a chlorophosphine with the enolate derived from an acetamide is a selective and convenient method for the preparation of (carbamoylmethyl)phosphines and consequently of the corresponding oxides and sulfides. The extension of this method to the preparation of the phosphinopyrazolonate $[Ph_2PC{=}C(O)N(Ph)N{=}C(Me)]Na$ has allowed the synthesis of new *P,O* chelate complexes. Further studies are in progress for the evaluation of the generality of the method described above.

Acknowledgment. This work benefitted from the use of facilities at the Laboratoire de Chimie Minérale et Analytique (Prof. Leroy, EHICS). We thank Dr. L. Toupet (Université de Rennes) for interesting discussion about the X-ray data and a reviewer for useful advice.

Supplementary Material Available: Tables S1–S5, containing complete crystallographic data, bond distances, bond angles, thermal parameters, and H atom coordinates for compound **12** (6 pages). Ordering information is given on any current masthead page.

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