prepared sample of monomer **3** was heated at 145 °C for 2 h in a sealed tube. Heating of **7** under a dynamic vacuum, as described above for **2**, resulted only in sublimation of **7**; no formation of the monomer **3** was observed.

Acknowledgment. We thank the U.S. Office of Naval Research, the Robert A. Welch Foundation, and the U.S. Army Research Office for generous financial support of this research.

Registry No. 1, 85336-22-7; **2**, 86563-48-6; **3**, 86563-49-7; **4**, 86563-50-0; **5**, 86563-51-1; **6**, 86563-52-2; **7**, 86563-53-3.

Complexes of Functional Phosphines. 6.[1] Five-Membered Palladium or Platinum Metallocycles Resulting from Nucleophilic Attack of α-Phosphino Carbanions on Organonitriles. Synthesis and Crystal Structure of *trans*-$\overline{\text{Pt[Ph}_2\text{PC(COOC}_2\text{H}_5\text{)C(Ph)NH}}]_2$ and $\text{Pd}(\overline{\text{C N}})\text{Cl}[\mu\text{-Ph}_2\text{PCH}_2\text{C}(\overline{\text{NH)C(CN)PPh}_2]\text{Pd}}(\overline{\text{C N}})$ $[\overline{\text{C N}} = o\text{-C}_6\text{H}_4\text{CH}_2\text{N(CH}_3)_2]$

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Received February 24, 1983

Reaction of 2 equiv of $\text{Li(Ph}_2\text{PCHY)}$ (Y = CN, COOEt) with $\text{PtCl}_2\text{(PhCN)}_2$ proceeds via nucleophilic attack on the coordinated nitriles afforded *trans*-$\overline{\text{Pt[Ph}_2\text{PC(Y)C(Ph)NH}}]_2$ (Y = CN, **1**; Y = COOEt, **2**). The crystal and molecular structure of **2** has been determined by X-ray diffraction methods. The compound crystallizes in the space group $P2_1/c$ of the monoclinic system with two formula units in a cell of dimensions a = 10.064 (3) Å, b = 23.272 (3) Å, c = 8.964 (1) Å, and β = 77.28 (1)°. The structure has been refined by least-squares methods to a final value of the conventional R factor of 0.047 on the basis of 3163 independent intensities. The molecule is centrosymmetric. The coordination about platinum is square planar, and there are only small deviations from planarity in the two metallocycles. The Pt–P bonds (2.280 (3) Å) and the Pt–N bonds (1.992 (8) Å) fall in a normal range; the shortness of the C(Ph)N bonds (1.32 (1) Å) suggests electron delocalization within the $\overset{\frown}{\text{P N}}$ chelate. An isoelectronic unsaturated metallocycle was found in $\text{Pd}(\overline{\text{C N}})\text{Cl}[\mu\text{-Ph}_2\text{PCH}_2\text{C}(\overline{\text{NH)C(CN)PPh}_2]\text{Pd}}(\overline{\text{C N}})$ (**5**; $\overline{\text{C N}}$ = $o\text{-C}_6\text{H}_4\text{CH}_2\text{N(CH}_3)_2$), the formation of which is interpreted as resulting from nucleophilic attack of the uncoordinated nitrile in the complex $(\overline{\text{C N}})\text{Pd(Cl)Ph}_2\text{PCH}_2\text{CN}$ by "$(\overline{\text{C N}})\text{Pd(Ph}_2\text{PCHCN)}$" (**6**), itself generated by reaction of $[(\overline{\text{C N}})\text{Pd}(\mu\text{-Cl})]_2$ with 2 equiv of $\text{Li(Ph}_2\text{PCHCN)}$. The structure of complex **5**·$2\text{CH}_2\text{Cl}_2$ was determined by single-crystal X-ray diffraction methods and refined to conventional R = 0.024. The compound crystallizes in the monoclinic crystal system of space group $P2_1$ with a = 10.234 (7) Å, b = 23.743 (10) Å, c = 10.663 (7) Å, β = 107.06 (2)°, and Z = 2. The molecule consists of two $(\overline{\text{C N}})\text{Pd}$ cyclopalladated moieties linked by the bridging six-electron donor multifunctional anionic ligand $\mu\text{-[Ph}_2\text{P(1)CH}_2\text{C(NH}^-\text{)CH(CN)P(2)Ph}_2]$. This original ligand is P(1) bonded to Pd(1) [Pd(1)–P(1) = 2.255 (2) Å] and (P(2),N) bonded in a chelate manner to Pd(2) [Pd(2)–P(2) = 2.239 (2), Pd(2)–N(3) = 2.092 (6) Å]. The coordination about Pd(1) is completed by a Cl ligand [Pd(1)–Cl = 2.405 (2) Å], trans with respect to P(1). The $\overline{\text{P(2)N}}$ unsaturated chelating moiety about Pd(2) is characterized by a short C(2)N(3) bond (1.30 (1) Å) resembling the situation found in **2**. The electron delocalization in **2** and **5** is related to the structural and spectroscopic data of the molecules. Spectroscopic (IR and ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR) data in solution are consistent with the solid-state structure of the new compounds.

Introduction

The coordination properties of functional phosphines $\text{R}_2\text{P}\sim\text{Y}$ toward transition metals attract considerable interest because of the structural features, the reactivity, and catalytic applications of the resulting complexes.[3-12] One of the obvious parameters controlling the bonding modes of the ligand is the nature of the function Y. For example, we have recently shown that (diphenylphosphino)aceto-

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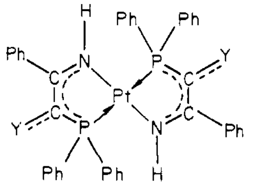
0276-7333/83/2302-1410$01.50/0

nitrile, Ph_2PCH_2CN (L^1), and ethyl (diphenylphosphino)acetate, $Ph_2PCH_2C(O)OC_2H_5$ (L^2), can behave either as monodenate (for L^1 and L^2) or chelate (for L^2) ligands toward a transition metal or as a bridging ligand (L^1) between two metal atoms.[1,3,6] For a given ligand, the bonding fashion encountered will, of course, depend upon the nature of the reacting metal center and of its ancillary ligands. A wider range of complexes and structural types was observed when using instead of L^1 or L^2 their corresponding α-carbanions $Li[Ph_2PCHCN]$ and $Li[Ph_2PCHC(O)OC_2H_5]$, respectively.[3,13] This introduces a third functionality into the ligand besides the phosphorus lone pair and the Y group. With these carbanions, bridging [with $(L^1)^-$ or $(L^2)^-$] or chelating [with $(L^2)^-$] bonding modes have been described in which the three functions available on the ligand are involved and contribute markedly to the structure adopted by the resulting complexes.[3]

In the course of these studies, we have discovered the unprecedented reaction of these α-phosphino functional carbanions with a coordinated organonitrile ligand. Thus, in a preliminary communication,[14] we have described the reaction of $(L^1)^-$ and $(L^2)^-$ with $PtCl_2(PhCN)_2$, leading to the platinum(II) bis(chelate) complexes *trans*-$\overline{\mathrm{Pt[PPh_2C(Y)C(Ph)NH}}]_2$ (Y = CN or $COOC_2H_5$), according to eq 1. In this paper, we wish to report the full data on the crystal structure of 2. We also present the crystal structure of a new dinuclear Pd(II) complex, obtained unexpectedly in the reaction of $[Pd(\overline{C\,N})(\mu\text{-}Cl)]_2$ ($\overline{C\,N}$ = $o\text{-}C_6H_4CH_2N(CH_3)_2$) with $(L^1)^-$.

$PtCl_2(PhCN)_2 + 2Li[Ph_2PCHY] \longrightarrow$



+ 2LiCl (1)

1, Y = CN
2, Y = $C(O)OC_2H_5$

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under argon. Solvents were distilled under argon from sodium benzophenone ketyl prior to use except dichloromethane, chlorobenzene, and acetone, which were dried and distilled over P_2O_5. Argon (Air Liquide purified grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water.

Elemental analysis of C, H, and N were performed by the Service Central de Microanalyses du CNRS.

Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer as KBr pellets (unless otherwise specified).

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 90.00 and/or 250.00, 62.86, and 36.43 MHz, respectively, on a FT-Brucker WH-90 or Cameca 250 instrument. Proton and carbon chemical shifts are positive downfield relative to external Me_4Si. Positive phosphorus chemical shifts indicate a downfield position relative to H_3PO_4.

Mass spectra for compounds 1 and 2 were measured on a Thompson THN 208 mass spectrometer (EI, 70 eV, 8 kV) by Dr. G. Teller (Université Louis Pasteur).

B. Syntheses. Ligands. Ph_2PCH_2CN (L^1) and $Ph_2PCH_2C(O)OC_2H_5$ (L^2) were reported earlier.[6] Standard solutions of the α-phosphino carbanions $[Ph_2PCHCN]^-$ and $[Ph_2PCHC(O)OC_2H_5]^-$, A and B, respectively, in THF were prepared by the method described previously where 50 mL of solution A and B contain in theory 5 mmol of functional carbanion (unreacted L^1 or L^2 is always present due to incomplete lithiation).[3]

Complexes. $PtCl_2(PhCN)_2$[15] and $[Pd(\overline{C\,N})(\mu\text{-}Cl)]_2$[16] [($\overline{C\,N}$) = $o\text{-}C_6H_4CH_2N(CH_3)_2$] were prepared according to literature methods.

***trans*-$\overline{\mathrm{Pt[Ph_2PC(CN)C(Ph)NH}}]_2$ (1).** To a stirred suspension of $PtCl_2(PhCN)_2$ (0.472 g, 1.0 mmol) in THF (25 mL) was added at 0 °C 20 mL of solution A. Rapid dissolution occurred, and after ca. 0.2 h the solution became turbid. After 1 h of stirring the yellow-green air-stable product 1 was collected, washed with THF (20 mL), and dried in vacuo (0.458 g, 54%). Despite its low solubility, 1 can be recrystallized from acetone/hexane or CH_2Cl_2/hexane: mp ≃300 °C slow dec; mass spectrum (70 eV), *m/e* (relative intensity) 849 (M based on ^{195}Pt, 100%; M(calcd) 849.7824); IR ν(NH) 3310 (mw), ν(CN) 2170 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.2–7.9 (aromatic protons); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 34.5 (s with ^{195}Pt satellites, $^1J(PtP)$ = 2657 Hz). Anal. Calcd for $C_{42}H_{32}N_4P_2Pt$: C, 59.36; H, 3.80; N, 6.60. Found: C, 59.38; H, 3.64; N, 7.20.

***trans*-$\overline{\mathrm{Pt[Ph_2PC(COOC_2H_5)C(Ph)NH}}]_2$ (2).** To a stirred suspension of $PtCl_2(PhCN)_2$ (0.472 g, 1.0 mmol) in THF (25 mL) was added at 0 °C 20 mL of solution B. After 1 h of stirring, pentane was added and the resulting yellow product was filtered and washed with toluene. Air-stable 2 was then recrystallized from CH_2Cl_2/hexane (0.519 g, 55%). Suitable single crystals for X-ray diffraction were obtained from acetone/*n*-hexane at 0 °C: mp 268–271 °C; mass spectrum (70 eV), *m/e* relative intensity) 943 (M based on ^{195}Pt, 100%; M(calcd) 943.8906); IR ν(NH) 3388 (mw), ν(CO) = 1678 (w), 1650 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.66 (3 H, t, CH_3, ^3J = 7.3 Hz), 3.71 (2 H, q, CH_2, ^3J = 7.3 Hz), 7.1–8.0 (15 H, aromatic protons); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 36.0 (s with ^{195}Pt satellites, $^1J(PtP)$ = 2524 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 13.76 (s, CH_2CH_3), 58.35 (s, CH_2CH_3), 186 (t, C═O, $^{2+4}J(PC)$ ≃ 24 Hz). Anal. Calcd for $C_{46}H_{42}N_2O_4P_2Pt$: C, 58.53; H, 4.49; N, 2.97. Found: C, 58.49; H, 4.18; N, 2.75.

$Pd(\overline{C\,N})Cl[\mu\text{-}Ph_2PCH_2C(\overline{NH)C(CN)PPh_2]}Pd(\overline{C\,N})$ (5). This compound was obtained in variable amounts (yield 20–30%) on adding at −10 °C 40 mL of solution A to a stirred suspension of $[Pd(\overline{C\,N})(\mu\text{-}Cl]_2$ (1.104 g, 2.0 mmol) in THF (50 mL). This solution was stirred for 0.5 h and pentane added, affording crystals of $Pd(\overline{C\,N})(\mu\text{-}Cl)[\mu\text{-}Ph_2P\overline{CH(CN)]}Pd(\overline{C\,N})$ (3) (see text). After isolation of 3 and further addition of pentane, yellow-green crystals of 5 precipitated. These were recrystallized from CH_2Cl_2/pentane, affording stable pale yellow crystals of the solvate $5{\cdot}2CH_2Cl_2$: mp 168 °C dec; IR ν(NH) 3285 (s), ν(CN) 2158 (s). ^1H NMR (CD_2Cl_2) δ 2.86 (6 H, d, $N(CH_3)_2$, $^4J(PH)$ = 2.6 Hz), 3.02 (6 H, d, $N(CH_3)_2$, $^4J(PH)$ = 2.2 Hz), 3.99–4.09 (6 H, superposition of several multiplets, unresolved signals), 6.0–8.0 (28 H, aromatic protons); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.3 (s, 1 P), 44.2 (s, 1 P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 35.97 (d, PC, $^1J(PC)$ = 30 Hz), 36.21 (d, PC, $^1J(PC)$ = 29 Hz), 51.53 (s, $N(CH_3)_2$), 51.69 (s, $N(CH_3)_2$), 73.17 (s, NCH_2), 73.75 (s, NCH_2). Anal. Calcd for $C_{48}H_{51}Cl_5N_4P_2Pd_2$: C, 50.75; H, 4.53; N, 4.93. Found: C, 50.80; H, 4.50; N, 4.99.

C. Collection of the X-ray Data and Structural Refinements. The X-ray crystal and molecular structure of compound 2 was determined by Y. D. and that of compound 5 by J. F.

Compound 2. Suitable single crystals of 2 were obtained from acetone/*n*-hexane at 0 °C. A parallelepiped crystal 0.012 × 0.012 × 0.020 cm was mounted in a Lindeman glass capillary. Intensity data were collected (at room temperature, range 6° < 2θ < 60°

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Table I. Fractional Atomic Coordinates ($\times 10^4$) and Their Estimated Standard Deviations for 2

atom	*x*	*y*	*z*
Pt	0000 (0)	5000 (0)	5000 (0)
P	−1260 (2)	4345 (1)	4014 (3)
O(1)	177 (8)	2760 (3)	3450 (10)
O(2)	−1708 (8)	3132 (3)	2904 (10)
C(1)	−98 (9)	3765 (4)	3581 (11)
C(2)	1218 (9)	3906 (4)	3723 (10)
C(3)	−629 (10)	3203 (5)	3258 (12)
C(4)	−270 (0)	2194 (0)	3027 (0)
C(5)	728 (0)	1786 (0)	3031 (0)
C(6)	2438 (9)	3548 (4)	3143 (10)
C(7)	2678 (13)	3290 (5)	1740 (13)
C(8)	3892 (17)	2999 (6)	1177 (17)
C(9)	4863 (15)	2948 (6)	2029 (23)
C(10)	4651 (13)	3204 (6)	3408 (21)
C(11)	3433 (10)	3491 (5)	3998 (14)
C(12)	−2766 (8)	4115 (4)	5397 (10)
C(13)	−3935 (10)	4447 (5)	5655 (12)
C(14)	−5046 (11)	4309 (6)	6792 (14)
C(15)	−5017 (12)	3836 (5)	7699 (13)
C(16)	−3876 (13)	3508 (6)	7473 (14)
C(17)	−2752 (12)	3640 (5)	6337 (13)
C(18)	−1878 (9)	4596 (4)	2361 (10)
C(19)	−1382 (11)	5104 (5)	1171 (12)
C(20)	−1799 (14)	5297 (7)	359 (16)
C(21)	−2702 (16)	4985 (10)	−193 (13)
C(22)	−3256 (18)	4495 (8)	508 (17)
C(23)	−2804 (15)	4282 (6)	1785 (15)
N	1434 (8)	4409 (3)	4310 (9)
H(7)	1938 (135)	3290 (58)	1208 (151)
H(8)	4035 (146)	2778 (63)	222 (171)
H(9)	5712 (153)	2726 (65)	1585 (164)
H(10)	5412 (147)	3157 (62)	4018 (160)
H(11)	3310 (124)	3683 (55)	5017 (144)
H(13)	−3949 (114)	4789 (49)	5004 (135)
H(14)	−5897 (132)	4569 (56)	6966 (146)
H(15)	−5851 (126)	3360 (57)	8529 (144)
H(16)	−3820 (133)	3138 (59)	8059 (154)
H(17)	−1906 (124)	3413 (54)	6195 (137)
H(19)	−719 (124)	5338 (53)	2072 (141)
H(20)	−1449 (143)	5712 (64)	−60 (160)
H(21)	−3024 (144)	5154 (67)	−1092 (170)
H(22)	−4092 (154)	4286 (67)	121 (175)
H(23)	−3086 (138)	3853 (62)	2152 (156)
H(N)	2429 (116)	4495 (49)	4240 (126)

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Their Estimated Standard Deviations for $5 \cdot 2CH_2Cl_2$

atom	*x*	*y*	*z*
Pd(1)	9849.3 (4)	5000.0 (0)	8136.6 (4)
Pd(2)	7582.9 (4)	7145.3 (2)	6737.2 (4)
Cl	11542 (2)	5729 (1)	8425 (2)
Cl(52)[a]	3315 (3)	7276 (1)	−882 (2)
Cl(53)[a]	1582 (3)	7398 (2)	6484 (4)
Cl(55)[a]	5286 (3)	4931 (1)	−582 (3)
Cl(56)[a]	5498 (3)	6010 (1)	8231 (3)
P(1)	9142 (1)	5099 (1)	5936 (1)
P(2)	6841 (1)	7054 (1)	4553 (1)
N(3)	8819 (5)	6468 (2)	6583 (5)
N(6)	7789 (7)	6174 (3)	1975 (5)
N(31)	10355 (5)	4867 (2)	10233 (5)
N(41)	8415 (5)	7253 (2)	8825 (4)
C(1)	9657 (6)	5772 (3)	5320 (6)
C(2)	8778 (6)	6259 (2)	5437 (6)
C(4)	7865 (6)	6490 (3)	4273 (5)
C(5)	7829 (7)	6311 (3)	3004 (6)
C(7)	9918 (6)	4586 (3)	5108 (6)
C(8)	9225 (7)	4180 (3)	4263 (6)
C(9)	9906 (8)	3798 (3)	3713 (7)
C(10)	11261 (9)	3820 (3)	3966 (7)
C(11)	11991 (7)	4228 (3)	4786 (7)
C(12)	11319 (7)	4611 (3)	5362 (7)
C(13)	7301 (6)	5101 (3)	5130 (5)
C(14)	6414 (6)	5137 (3)	5889 (6)
C(15)	5025 (7)	5198 (4)	5314 (7)
C(16)	4530 (7)	5211 (3)	3969 (8)
C(17)	5358 (7)	5172 (3)	3207 (7)
C(18)	6774 (7)	5110 (3)	3777 (6)
C(19)	7162 (6)	7637 (3)	3568 (6)
C(20)	8500 (7)	7719 (3)	3529 (6)
C(21)	8790 (8)	8190 (4)	2856 (7)
C(22)	7803 (11)	8557 (3)	2291 (7)
C(23)	6432 (10)	8479 (3)	2294 (7)
C(24)	6103 (8)	8017 (3)	2926 (6)
C(25)	5046 (6)	6871 (3)	3840 (6)
C(26)	4509 (7)	6775 (3)	2508 (7)
C(27)	3141 (8)	6612 (4)	1996 (8)
C(28)	2349 (7)	6557 (4)	2827 (9)
C(29)	2893 (8)	6631 (5)	4138 (8)
C(30)	4253 (7)	6796 (4)	4643 (7)
C(32)	11489 (8)	4458 (3)	10595 (7)
C(33)	10733 (9)	5377 (4)	11045 (7)
C(34)	9134 (7)	4621 (4)	10435 (6)
C(35)	8531 (6)	4203 (3)	9371 (6)
C(36)	7904 (8)	3716 (4)	9588 (7)
C(37)	7372 (8)	3343 (4)	8590 (8)
C(38)	7502 (8)	3442 (3)	7377 (8)
C(39)	8155 (7)	3930 (3)	7137 (7)
C(40)	8688 (6)	4319 (3)	8135 (6)
C(42)	9025 (8)	6752 (4)	9564 (7)
C(43)	9448 (7)	7700 (3)	9074 (7)
C(44)	7217 (7)	7449 (3)	9260 (6)
C(45)	6398 (6)	7860 (3)	8276 (6)
C(46)	5675 (7)	8307 (3)	8634 (7)
C(47)	4941 (7)	8659 (3)	7725 (7)
C(48)	4846 (7)	8588 (3)	6402 (7)
C(49)	5554 (6)	8159 (3)	6058 (6)
C(50)	6363 (6)	7781 (3)	6956 (5)
C(51)[a]	3060 (11)	7172 (6)	−2519 (10)
C(54)[a]	5139 (8)	5657 (4)	−453 (8)

[a] These atoms correspond to the two CH_2Cl_2 solvent molecules.

and variable scan speed) on a Nonius CAD 4 automatic diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). Crystal data: $C_{46}H_{42}N_2O_4P_2Pt$, mol wt 943.9, monoclinic, a = 10.064 (3) Å, b = 23.272 (3) Å, c = 8.964 (1) Å, β = 77.28 (1)°, V = 2048.0 (6) Å^3, Z = 2, d(calcd) = 1.53 g cm^{-3}, μ = 37 cm^{-1}, F_{000} = 944, space group $P2_1/c$. No intensity decay was observed during the data collection period, as shown by the systematic measure of three standard reflections after every 50 reflections. Corrections were applied for Lorentz and polarization effects. Absorption corrections were omitted in view of the low linear absorption coefficient.

The structure was solved by Patterson and Fourier methods,[17] using 3163 reflections having $I > \sigma(I)$; aromatic H atoms were located by difference Fourier sections and introduced in the calculation and only their atomic coordinates were refined. Their thermal parameters were fixed to the value of the corresponding carbon atoms. Refinements by full-matrix least squares (all non-hydrogen anisotropic) have proceeded to R = 0.047, using the Busing et al. method.[17] A final difference map revealed no significant maxima.

The final fractional atomic coordinates are given in Table I. The final thermal parameters for all atoms as well as a table listing the observed and calculated structure factor amplitudes of the reflections used in the refinement are available as supplementary material.[19]

Compound 5. Suitable single crystals of the solvate $5 \cdot 2CH_2Cl_2$ were obtained by slow crystallization from dichloromethane/pentane solutions at room temperature.

A systematic search in the reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of

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(18) Sheldrick, G. M., SHELX Crystallographic Calculation Program, University of Göttingen, West Germany.

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

Table III. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-$Pt[Ph_2PC(COOC_2H_5)C(Ph)NH]_2$ (2)

Bond Distances

Pt-N	1.992 (8)	C(4)-C(5)	1.38 (1)	C(14)-C(15)	1.37 (2)
Pt-P	2.280 (3)	C(2)-C(6)	1.48 (1)	C(15)-C(16)	1.36 (2)
P-C(1)	1.773 (9)	C(6)-C(7)	1.37 (2)	C(16)-C(17)	1.38 (2)
P-C(12)	1.818 (8)	C(7)-C(8)	1.39 (2)	C(17)-C(12)	1.39 (1)
P-C(18)	1.824 (10)	C(8)-C(9)	1.37 (2)	C(18)-C(19)	1.38 (2)
N-C(2)	1.32 (1)	C(9)-C(10)	1.35 (3)	C(19)-C(20)	1.41 (2)
C(1)-C(2)	1.39 (1)	C(10)-C(11)	1.40 (2)	C(20)-C(21)	1.34 (2)
C(1)-C(3)	1.46 (1)	C(11)-C(6)	1.39 (2)	C(21)-C(22)	1.36 (3)
C(3)-O(2)	1.21 (1)	C(12)-C(13)	1.38 (1)	C(22)-C(23)	1.41 (2)
C(3)-O(1)	1.34 (1)	C(13)-C(14)	1.38 (1)	C(23)-C(18)	1.37 (2)
O(1)-C(4)	1.47 (1)				

Bond Angles

P-Pt-N	81.0 (2)	C(1)-C(3)-O(2)	123.9 (10)	C(13)-C(14)-C(15)	120 (1)
Pt-N-C(2)	124.4 (6)	C(3)-O(1)-C(4)	115.5 (8)	C(14)-C(15)-C(16)	119 (1)
Pt-P-C(1)	101.4 (3)	O(1)-C(4)-C(5)	110.6 (3)	C(15)-C(16)-C(17)	121 (1)
Pt-P-C(12)	112.6 (3)	O(1)-C(3)-O(2)	122.0 (10)	C(16)-C(17)-C(12)	121 (1)
Pt-P-C(18)	114.6 (3)	C(2)-C(6)-C(7)	122.5 (10)	C(17)-C(12)-C(13)	117.5 (8)
C(1)-P-C(12)	109.8 (4)	C(6)-C(7)-C(8)	121 (1)	C(17)-C(12)-P	122.0 (7)
C(1)-P-C(18)	113.0 (4)	C(7)-C(8)-C(9)	121 (1)	P-C(18)-C(19)	119.0 (8)
C(12)-P-C(18)	105.5 (4)	C(8)-C(9)-C(10)	119 (1)	C(18)-C(19)-C(20)	120 (1)
P-C(1)-C(3)	118.3 (7)	C(9)-C(10)-C(11)	121 (2)	C(19)-C(20)-C(21)	119 (1)
P-C(1)-C(2)	113.2 (7)	C(10)-C(11)-C(16)	121 (1)	C(20)-C(21)-C(22)	122 (1)
C(1)-C(2)-N	119.1 (8)	C(11)-C(6)-C(7)	117 (1)	C(21)-C(22)-C(23)	120 (2)
C(1)-C(2)-C(6)	124.4 (8)	C(11)-C(6)-C(2)	120.0 (9)	C(22)-C(23)-C(18)	119 (1)
N-C(2)-C(6)	116.3 (8)	P-C(12)-C(13)	120.1 (7)	C(23)-C(18)-C(19)	120 (1)
C(1)-C(3)-O(1)	114.1 (10)	C(12)-C(13)-C(14)	121 (1)	C(23)-C(18)-P	121.0 (8)

$5 \cdot CH_2Cl_2$ belong to the monoclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu Kα radiation ($\lambda = 1.5418$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{48}H_{51}Cl_5N_4P_2Pd_2$, mol wt 1136.0, $a = 10.234$ (7) Å, $b = 23.743$ (10) Å, $c = 10.663$ (7) Å, $\beta = 107.06$ (2)°, $V = 2477$ (7) Å^3, $Z = 2$, d(calcd) = 1.52 g cm^{-3}, d(obsd) = 1.50 ± 0.02 g cm^{-3}, space group $P2_1$, $\mu = 94.15$ cm^{-1}, $F_{000} = 1148$.

A spherical crystal of 0.20-mm diameter was sealed in a Lindeman glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P852M computer, using graphite-monochromated Cu Kα radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\omega/2\theta$ flying step-scan used was $\Delta\omega = 1.10° +$ (Cu Kα_1, α_2 splitting) with a step width of 0.05° and a scan speed of 0.025° s^{-1}. A total of 3577 hkl and $\bar{h}kl$ reflections were recorded ($3° < 2\theta < 57°$). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used,[20] with the exception of a local data reduction program. Three standard reflections measured every hour during the entire data collection period showed no significant change in the measured intensities. These were corrected for Lorentz, polarization, and absorption factors, the latter computed by interpolation of ref 21 (transmission factors between 0.18 and 0.25). From the 3577 data collected, a unique data set of 3033 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After the refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 8 Å^2 but not refined. Full-matrix least-squares refinement converged to conventional $R = 0.024$ and $R_w = 0.03$ ($w = [\sigma_{\text{count}}^2 + (PI)^2]^{-1}$). The standard error in an observation of unit weight was 1.23 for $P = 0.04$. A final difference map revealed no significant maxima.

The final fractional atomic coordinates are given in Table II. Thermal parameters for all non-hydrogen atoms and observed and calculated structure factor amplitudes of the reflections used in the refinement are available as supplementary material.[19]

Results and Discussion

***trans*-$Pt[Ph_2PC(Y)C(Ph)NH]_2$ [Y = CN, 1; Y = C(O)OC$_2$H$_5$, 2].** The formula and molecular structure of complexes 1 and 2 were established by a combination of IR, ^{1}H and ^{31}P NMR, and mass spectroscopy and single-crystal X-ray diffraction analyses (see Experimental Section). An ORTEP diagram of the molecular structure of 2 is shown in Figure 1. Bond distances and angles are listed in Table III and least-squares planes in Table IV.[19] The molecule is centrosymmetric, implying a square-planar coordination for the Pt atom. As suggested by the shortness of the C(2)–N bond (1.32 (1) Å) and by relatively low IR frequencies for the C≡N or the C=O group, an extensive electron delocalization within the chelate ligand may be postulated. The small deviations from planarity of the metallocycles are characterized by the dihedral angles given in Table IV.[19] The Pt–P distance (2.280 (3) Å) is found to be in the range usually observed in Pt(II) complexes having a *trans* R_3P–Pt–PR_3 arrangement.[30] The Pt–N< distance (1.992 (8) Å) is shorter than usual Pt←NR_3 bonds,[30] as expected from a possible participation to the bonding of the lone pair of the amido group in 2. The values found agree well with those observed in other Pt–amide bonds.[31] For complex 1, the ^1J(PPt) value is in agreement with[32] an analogous trans structure. Structural characteristics of the five-membered metallocycles in 2 are given in Table VII and compared with those of isoelectronic systems. Attempts to open the chelates by CH_3I have failed: no cleavage of the Pt–N bond was observed, in contrast to the Pt–Si bond of the related bis(chelate) *cis*-$[Pt(Ph_2PCH_2CH_2SiMe_2)_2]$ complex.[33] Because it was generally assumed that $PtCl_2(PhCN)_2$ has a cis structure, we described reaction 1 as occurring with isomerization since the isolated products have a trans structure, in so-

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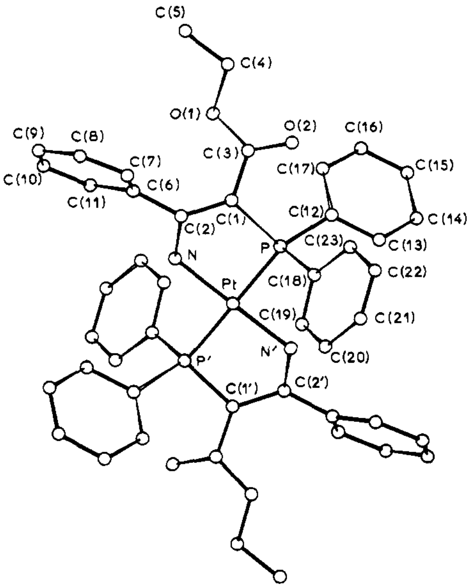


Figure 1. Molecular structure of *trans*-Pt[$\overline{\mathrm{Ph_2PC(CO_2Et)C(Ph)NH}}$]$_2$ (2).

lution (^{31}P NMR spectra) and in the solid state. In fact, the presence of both *cis*- and *trans*-PtCl$_2$(PhCN)$_2$ cannot be ruled out. Thus, an easy interconversion between these isomers has been established although no quantitative data seem available for this system in THF solution.[34] We have therefore no proof for either isomerization or retention of geometry of the complexes during reaction 1. It is noteworthy that, although PhCN is usually a good leaving group, the reaction described here does not lead to bischelated complexes of formula Pt(Ph$_2$PCHY)$_2$. Such a complex with Y = C(O)OC$_2$H$_5$ has previously been obtained via an other route and was shown to contain two stable five-membered rings.[3] In the case where Y = CN, such a complex would contain a strained three-membered $\overline{\mathrm{PtPC}}$ ring[22] and present very interesting properties by analogy with what has been found with Re,[23] Fe,[24-26] Ru,[27] Co,[26,28] Ir[29] in related structures.

We shall describe below the structure of a new complex the formation of which might have occurred via a three-membered $\overline{\mathrm{PdPC}}$ intermediate (see **6B**).

Pd($\overline{\mathrm{C\ N}}$)Cl[μ-Ph$_2$PCH$_2$$\overline{\mathrm{C(NH)C(CN)PPh_2]Pd}}$($\overline{\mathrm{C\ N}}$) (5). We described previously the reactions of the cyclometalated dinuclear Pd(II) complex [Pd($\overline{\mathrm{C\ N}}$)(μ-Cl)]$_2$ ($\overline{\mathrm{C\ N}}$ = 2-[(dimethylamino)methyl]phenyl-*C*,*N*, *o*-C$_6$H$_4$CH$_2$N(CH$_3$)$_2$) with (L^1)$^-$ and (L^2)$^-$.[3]

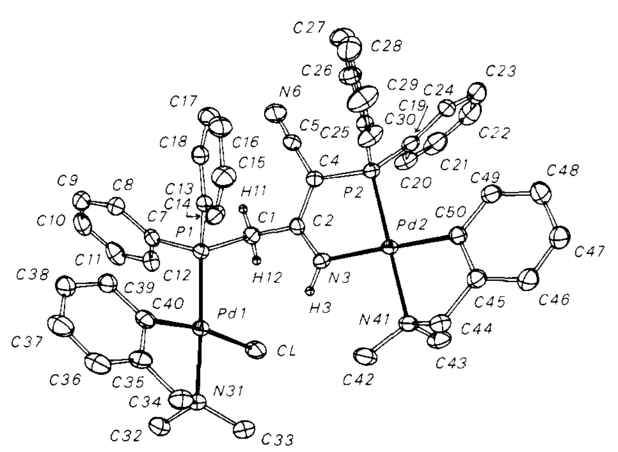
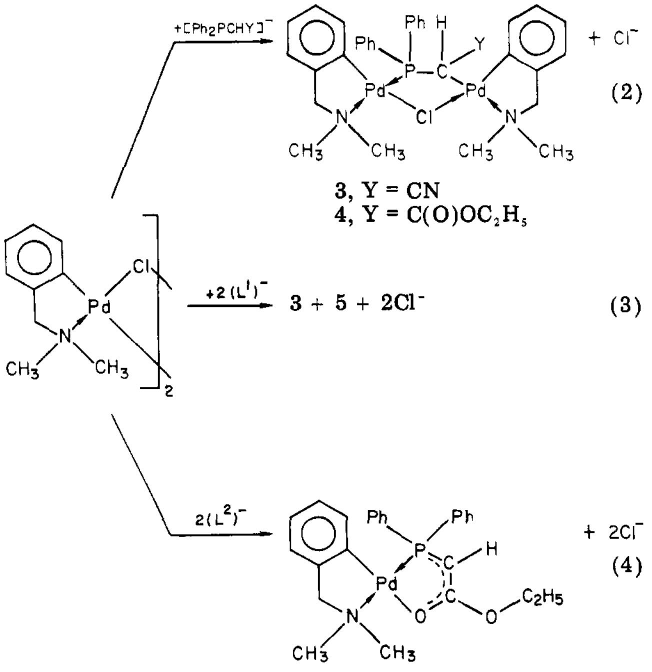


Figure 2. Molecular Structure of Pd($\overline{\mathrm{C\ N}}$)Cl[μ-Ph$_2$PCH$_2$$\overline{\mathrm{C(NH)C(CN)PPh_2]Pd}}$($\overline{\mathrm{C\ N}}$) (5). The two CH$_2Cl_2$ solvent molecules have been omitted for clarity.

Depending upon the stoichiometry used, we isolated mono- or dinuclear Pd(II) complexes with these ligands, according to eq 2–4. In complexes **3** and **4**, which were fully characterized,[13] the functional carbanion [L]$^-$ acts as a four-electron *bridging* ligand between the Pd atoms. In **7** on the other hand, [L^2]$^-$ is a four-electron donor *chelate*. This is based on its X-ray structure determination,[13] indicating that the five-membered ring is preferred to the triangulo $\overline{\mathrm{MPC}}$ structure which could have been envisaged instead (with an uncoordinated C(O)OC$_2$H$_5$ function). Complex **7** was shown in solution to be a reactive molecule, functioning as a reversible CO$_2$ carrier under ambient conditions.[3]



3, Y = CN
4, Y = C(O)OC$_2$H$_5$

7

Addition of 2 equiv of [L^1]$^-$ to [Pd($\overline{\mathrm{C\ N}}$)(μ-Cl)]$_2$ (eq 3) led to the dinuclear Pd(II) complex **3** (obtained in the reaction with 1 equiv of [L^1]$^-$, eq 2) and to another complex, **5**, which originally could not be structurally identified

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Table V. Selected Interatomic Distances (Å) and Angles (deg) in $5 \cdot 2CH_2Cl_2$

Bond Distances

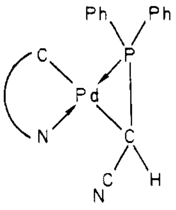
Pd(1)-P(1)	2.255 (2)	P(1)-C(13)	1.828 (7)	P(2)-C(25)	1.823 (7)
Pd(1)-Cl	2.405 (2)	P(1)-C(1)	1.862 (8)	Pd(2)-P(2)	2.239 (2)
Pd(1)-N(31)	2.167 (6)	C(1)-C(2)	1.49 (1)	Pd(2)-N(3)	2.092 (6)
Pd(1)-C(40)	2.001 (8)	C(2)-N(3)	1.30 (1)	Pd(2)-C(50)	2.015 (7)
N(31)-C(32)	1.47 (1)	C(2)-C(4)	1.42 (1)	Pd(2)-N(41)	2.151 (5)
N(31)-C(33)	1.47 (1)	C(4)-C(5)	1.41 (1)	N(41)-C(42)	1.45 (1)
N(31)-C(34)	1.44 (1)	C(5)-N(6)	1.13 (1)	N(41)-C(43)	1.46 (1)
C(34)-C(35)	1.49 (1)	P(2)-C(4)	1.777 (8)	N(41)-C(44)	1.51 (1)
P(1)-C(7)	1.814 (8)	P(2)-C(19)	1.825 (8)	C(44)-C(45)	1.49 (1)

Bond Angles

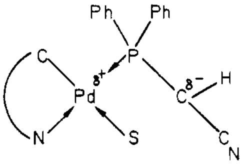
C(1)-Pd(1)-P(1)	93.32 (7)	C(1)-C(2)-N(3)	120.6 (6)	Pd(2)-P(2)-C(19)	117.5 (2)
C(1)-Pd(1)-C(40)	170.0 (2)	C(1)-C(2)-C(4)	118.8 (6)	Pd(2)-P(2)-C(25)	116.7 (2)
P(1)-Pd(1)-N(31)	91.5 (2)	C(2)-N(3)-Pd(2)	120.4 (5)	N(3)-Pd(2)-P(2)	82.6 (1)
P(1)-Pd(1)-C(40)	94.2 (2)	C(2)-C(4)-P(2)	114.3 (5)	N(3)-Pd(2)-C(50)	117.4 (2)
P(1)-Pd(1)-N(31)	174.8 (2)	C(2)-C(4)-C(5)	122.6 (5)	N(3)-Pd(2)-N(41)	96.1 (2)
C(40)-Pd(1)-N(31)	81.1 (3)	C(4)-C(5)-N(6)	178.8 (9)	P(2)-Pd(2)-C(50)	99.2 (2)
Pd(1)-P(1)-C(7)	112.4 (2)	C(4)-P(2)-Pd(2)	102.1 (2)	P(2)-Pd(2)-N(41)	176.3 (2)
Pd(1)-P(1)-C(13)	117.6 (2)	C(4)-C(2)-N(3)	120.5 (6)	C(50)-Pd(2)-N(41)	82.1 (2)
Pd(1)-P(1)-C(1)	114.7 (2)				
P(1)-C(1)-C(2)	113.3 (5)				

[a] Mean $C \underset{\cdot\cdot}{-} C$ distances in the phenyl rings bonded to P(1) and P(2) = 1.385 (4) Å. Mean $C \underset{\cdot\cdot}{-} C$ distances in the phenyl rings C(34)-C(40) and C(45)-C(50) = 1.375 (3).

but which has now been fully characterized (see below). It was suggested that 3 could result in this experiment from the reaction of the postulated[3] intermediate $[Pd(\overline{C\ N})(Ph_2PCHCN)]$ (**6**) with $[Pd(\overline{C\ N})(\mu\text{-}Cl)]_2$. This intermediate seems too reactive to be isolated, whereas its homologue **7** is stabilized by (P,O) chelation of $[L^2]^-$, a situation which cannot be encountered with $[L^1]^-$ for obvious geometrical reasons. In a separate experiment, it was found that **7** reacts with $[Pd(\overline{C\ N})(\mu\text{-}Cl)]_2$ to form **4**.[13] There were therefore some indications for the occurrence of **6** in the above described reactions. Although we do not know the structure of **6** in solution (structures **6B** or **6C** could be envisaged), a further argument supporting its formation is now available with the elucidation by X-ray diffraction of the molecular structure of complex **5**. The X-ray molecular structure of $5 \cdot CH_2Cl_2$ is shown in Figure 2 and a stereoscopic view in Figure 3,[19] and interatomic distances and angles are given in Table V, intra- and intermolecular contacts in Table V,[19] and least-squares planes in Table VI.[19] Complex **5** was recrystallized from dichloromethane/pentane, and two CH_2Cl_2 solvatation molecules per molecule of **5** were found in the crystal. They are hydrogen bonded and the crystal cohesion results from van der Waals interactions and hydrogen bonds from one molecule to a number of others.



6B



6C

S = donor solvent molecule

The molecule of **5** is composed of three fragments: two {2-[(dimethylamino)methyl]phenyl-*C*,*N*}palladium (($\overline{C\ N}$)Pd) moieties linked by the bridging tridendate six-electron donor anionic ligand $\mu\text{-}[Ph_2PCH_2C(NH^-){=}C(C{\equiv}N)PPh_2]$ (PNP). This original ligand is P bonded to Pd(1) (through P(1)) and (P, N) bonded in a chelate manner to Pd(2) (through P(2) and N(3)) (see Figure 2). We shall discuss below the possible reaction pathway to this new ligand.

The two palladium atoms are in distorted square-planar environments. Pd(1) is bonded to carbon C(40) and to nitrogen N(31) of a ($\overline{C\ N}$) chelate, a chloride ligand, and phosphorus P(1) of PNP, which is trans with respect to the nitrogen N(31). As seen from the distances to the mean plane PL1 in Table VI,[19] these five atoms are not coplanar (Figures 2 and 3[19]). This probably results from steric interactions within the molecule. Pd(2) is bonded to a ($\overline{C\ N}$) chelate, through C(50) and N(41), to the phosphorus P(2) and to nitrogen N(3) of the chelating side of PNP. The one-electron donor atoms C(50) and N(3) are trans to each other, as found around Pd(1) with C(40) and Cl. The deviations from planarity about Pd(2) are indicated by the distances of the corresponding atoms to the mean plane PL2 (Table VI).

The structure and bonding mode of the two $\overline{C\ N}$ chelates in **5** are very similar (see Table V) and resemble those found in other palladium complexes with this ligand.[3,35] In each Pd($\overline{C\ N}$) metallocycle, the nitrogen atom is out of the mean plane, on the same side as the palladium atom (Table VI[19]).

The part of the molecule around Pd(1) is typical for a phosphine type complex, with a Pd(1)–P(1) distance of 2.255 (2) Å (compare with 2.233 (6) in **4** and 2.242 (2) Å in **7**). The phosphorus atom in all ($\overline{C\ N}$) cyclometalated complexes is in a trans position with respect to the nitrogen atom of the chelate which is of lower trans influence than the σ-bonded carbon. The Pd(1)–Cl distance (2.405 (2) Å) is in the range usually found for such bonds trans to a σ-bonded carbon atom.[36] The part of the molecule around Pd(2) deserves more comments. Whereas the $\overline{C\ N}$ chelate is normal (vide supra) and the phosphorus atom P(2) trans to the nitrogen N(41) of $\overline{C\ N}$, the [P(2),N(3)] chelate is unique. It is isoelectronic and strongly related

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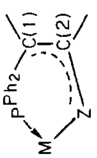
Table VII. Structural Data[a] for Five-Membered Unsaturated Metallocycles of the Type

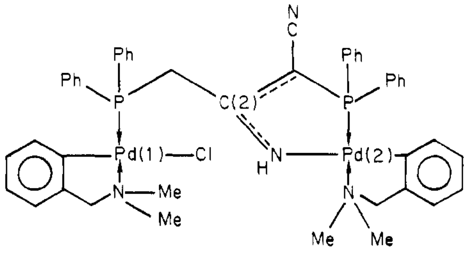


M = Ni, Pd, Pt

	nature of the substituent at			distances, Å					angles, deg					
M	C(1)	C(2)	nature of Z	M-P	P-C(1)	C(1)-C(2)	C(2)-Z	Z-M	Z-M-P	M-P-C(1)	P-C(1)-C(2)	C(1)-C(2)-Z	C(2)-Z-M	ref
Ni	H	Ph	O	2.168	1.769	1.365	1.313	1.914	86.5	99.3	113.8	122.1	118.9	8
Pd	H	OC_2H_5	O	2.242 (2)	1.751 (9)	1.37 (1)	1.27 (1)	2.117 (5)	83.8 (1)	100.5 (3)	114.2 (7)	126.8 (9)	114.4 (6)	3
Pd	CN	CH_2PPh_2- PdCl[$\overline{\mathrm{C\;N}}$]	NH	2.239 (2)	1.777 (8)	1.42 (1)	1.300 (9)	2.092 (6)	82.6 (1)	102.1 (2)	114.3 (5)		120.4 (5)	c
Pt	$C(O)OC_2H_5$	Ph	NH	2.280 (3)	1.773 (9)	1.39 (1)	1.32 (1)	1.992 (8)	81.0 (2)	101.4 (3)	113.2 (7)	119.1 (8)	124.4 (6)	c 32
Pt[b]	$(H)_2$	$(H)_2$	$Si(CH_3)_2$	2.345 (6) (av)				2.355 (8) (av)	83.3 (2)					

[a] One should keep in mind that these data are also dependent upon the nature of the other ligands bonded to M. [b] In this complex, the metallocycle is saturated. Available data are only given for comparison. [c] This work.

to the (P,N) chelate found in **1** and discussed above. (They only differ by the substituent at C(2)). The shortness of the C(2)-N(3) bond (1.30 (1) Å) and the relative shortness of the P(2)-C(4) bond (1.777 (8) Å) (compared to P(2)-C(19) and P(2)-C(25), average 1.824 (8) Å) together with the rather low IR frequency for the $C\equiv N$ group (2158 cm^{-1}) suggest an extensive electron delocalization within the (P,N) chelate of the type shown in **5**.



5

On the basis of these criteria, this electron delocalization seems even more pronounced than in **1** (vide supra). The C(2)-C(4) distance in **5** (1.42 (1) Å) compares with the C(1)-C(2) distance in **2** (1.39 (1) Å) and the P(2)-C(4) distance in **5** with the P-C(1) distance in **2** (1.773 (9) Å) (Tables III, V, and VII).

The covalent Pd(2)-N(3) bond (2.092 (6) Å) is shorter than the dative Pd(1)-N(31) and Pd(2)-N(41) bonds (average 2.159 Å). The Pd(2)-P(2) distance (2.239 (2) Å) is slightly shorter than the Pd(1)-P(1) distance (2.255 (2) Å). This is probably related to the chelate effect involving P(2), similar to that observed in **7** (Pd-P = 2.242 (2) Å).[3]

The C(5)-N(6) bond length of 1.13 (1) Å is consistent with a $C\equiv N$ triple bond, and the C(4)-C(5)-N(6) group is linear. The P(1)-C(1) bond length of 1.862 (8) Å is slightly longer than the P(2)-C(4) distance of 1.777 (8) Å, because of the electron delocalization involving the latter bond. The C(1)-C(2) distance of 1.49 (1) Å is normal for a C(sp^3)-C(sp^2) bond.[37]

The phenyl rings bonded to P(1) and P(2) have normal geometries, with an average P-phenyl distance of 1.822 (4) Å.

A comparison of structural data for a series of related five-membered bifunctional chelating systems is presented in Table VII.

The spectroscopic data collected for **5** in solution are consistent with its solid-state structure. The phosphino groups appear in the ^{31}P NMR at 40.3 and 44.2 ppm, in the range expected for coordinated phosphine ligands of this type.[3,6] The fact that P(1) and P(2) remain in solution bonded trans to the nitrogen atoms N(31) and N(41), respectively, is easily deduced from the observation of the coupling of the $N(CH_3)_2$ protons with phosphorus (^4J(PH) = 2.6 and 2.2 Hz, respectively).

The synthesis of **5** can now be easily explained. Since a standard solution (A) of the carbanion $(L^1)^-$ contains some phosphine L^1, the latter can react with [Pd($\overline{\mathrm{C\;N}}$)(μ-Cl)]$_2$ in a classical bridge splitting reaction, to afford the neutral Pd($\overline{\mathrm{C\;N}}$)ClL^1 complex.[3] The functional carbanion, on the other hand, would react with [Pd($\overline{\mathrm{C\;N}}$)(μ-Cl)]$_2$ to form the mononuclear intermediate[3] Pd($\overline{\mathrm{C\;N}}$)-(Ph_2PCHCN) (**6**) mentionned earlier in this paper. The carbon atom α to the phosphorus in **6** is still of carbanionic character. From the reaction of the carbanion-like inter-

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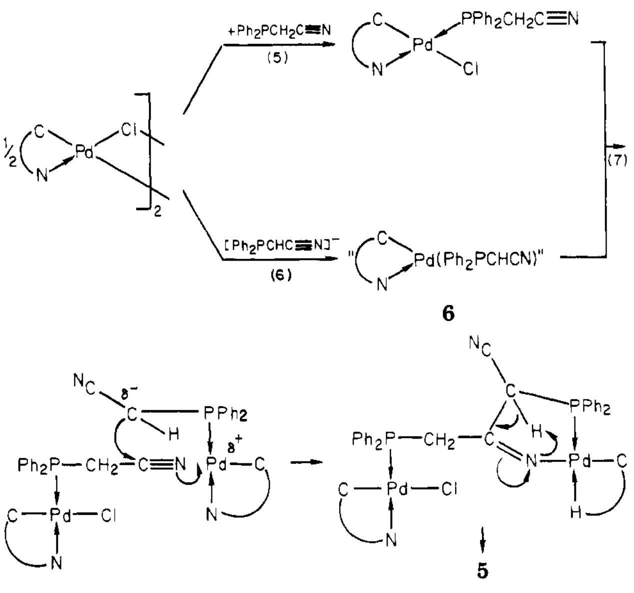
[37] Wilson, R. B.; de Meester, P.; Hodgson, D. J. *Inorg. Chem.* **1977**, *16*, 1498.

mediate 6 with the nitrile function of Pd($\overline{\mathrm{C\ N}}$)ClL^1 results the formation of 5. This reaction is strongly related to that described above between [L^1]$^-$ and the coordinated nitrile of PtCl$_2$(PhCN)$_2$ (eq 1). The differences reside in that (i) the carbanion is P coordinated in 6 (by contrast to (L^1)$^-$) and (ii) the attacked nitrile function is uncoordinated but connected to a metal via a phosphino group in Pd($\overline{\mathrm{C\ N}}$)ClL^1. The sequence of reactions shown in eq 5–7 accounts for these observations.



The possible structures of intermediate 6 formed in (eq 6) have been discussed above (structures **6B** and **6C**). After nucleophilic attack on the nitrile has occurred (eq 7), the H shift from C(4) to N(3) follows the same pattern as in the reaction leading to 1.[14] This gives rise in the IR to a ν(NH) vibration at 3285 cm^{-1}.

In conclusion, the reactions presented in this paper, namely, (i) nucleophilic attack of a carbanion on a coordinated organonitrile ligand and (ii) nucleophilic attack of a carbanionic metal complex on the free nitrile group of a functional phosphine complex, demonstrate the potential use of α-phosphino carbanions in synthetic coordination chemistry. They also illustrate the metal-assisted synthesis of new ligands since these reactions were performed within the coordination sphere of the metals involved.

Acknowledgment. Thanks are due to the CNRS for financial support and to A. Mitschler for collecting the X-ray data for 5.

Registry No. 1, 72910-27-1; **2**, 72910-26-0; **3**, 79079-79-1; 4, 77063-83-3; **5**, 86632-51-1; **7**, 79110-94-4; PtCl$_2$(PhCN)$_2$, 14873-63-3; [Pd($\overline{\mathrm{C\ N}}$)(M–Cl)]$_2$, 18987-59-2; Li[Ph$_2$PCHCN], 86632-52-2; Li[Ph$_2$PCHCOOC$_2$H$_5$], 86632-53-3.

Supplementary Material Available: Tables of least-squares planes (Tables IV and VI), anisotropic thermal parameters (Tables VIII and IX), and observed and calculated structure factors for 2 and 5·2CH$_2$Cl$_2$ (Tables X and XI) and intra- and intermolecular contacts in 5·CH$_2$Cl$_2$ (Table V) and stereoscopic view of 5 (Figure 3) (46 pages). Ordering information is given on any current masthead page.

Reactivity of [HFe$_3$(CO)$_{11}$]$^-$ toward Ethylene. Synthesis and Crystal Structure of Tetraphenylphosphonium [μ_3-Propionyl-*C*(*Fe*^{1},*Fe*^{2}),*O*(*Fe*^{1},*Fe*^{3})]nonacarbonyl-*triangulo*-triferrate. Study of Its Reactivity toward CO, P(C$_6$H$_5$)$_3$, H$_2$, and Proton

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Received February 3, 1983

Reaction of the cluster anion [HFe$_3$(CO)$_{11}$]$^-$ with ethylene at room temperature gives the trinuclear cluster anion [Fe$_3$(CO)$_9$(μ_3-COC$_2$H$_5$)]$^-$. The structure of this cluster anion has been determined by X-ray diffraction study of the tetraphenylphosphonium salt 1. The latter is monoclinic of space group $C2/c$ with a = 18.813 (3) Å, b = 17.641 (4) Å, c = 22.551 (4) Å, β = 106.34 (2)°, and Z = 8. The structure has been solved and refined to R and R_w values of 0.054 and 0.060, respectively, using 3583 reflections. A μ_3 mode of bonding is shown for the acyl group. This is the first case where this mode of bonding results from the direct action of an alkene on a cluster unit. Reactivity of 1 toward CO and P(C$_6$H$_5$)$_3$ is attended by complete rupture of the cluster unit into Fe(CO)$_4$COC$_2$H$_5$$^-$ (CO case) or Fe(CO)$_{5-n}$[P(C$_6$H$_5$)$_3$]$_n$ (n = 1, 2). 1 gives a mixture of ethane and propanol under hydrogen pressure, which suggests an alkyl/acyl equilibrium in the cluster under the conditions of the reaction. Protonation of 1 gives HFe$_3$(CO)$_9$(μ_3-COC$_2$H$_5$).

Introduction

We have recently shown that the [HFe$_3$(CO)$_{11}$]$^-$ anion reacts readily with alkynes with preservation of trinuclear iron unit.[1] Furthermore, this anion has a reactivity that compares well with the known reactivity of ruthenium and osmium trinuclear clusters.[2] These results are quite unexpected with respect to the known lability of metal–metal bonds for the first-row period of transition metals.

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[1] Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

[2] Deeming, A. J. "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: London, 1980; p 391.

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