

1,8-Bis(diphenylphosphino)anthracene and Metal Complexes¹⁾

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The title compound **4** was synthesized from dipotassium 1,8-anthracenedisulfonate (**9**) and potassium diphenylphosphide (Ph_2PK). On reaction of **4** with nickel(II) chloride and bis(benzonitrile)palladium(II) chloride, cyclometallation of the C–H bond in anthracene 9-position led to the square-planar chelate complexes **11** and **13**, respectively. In the case of the

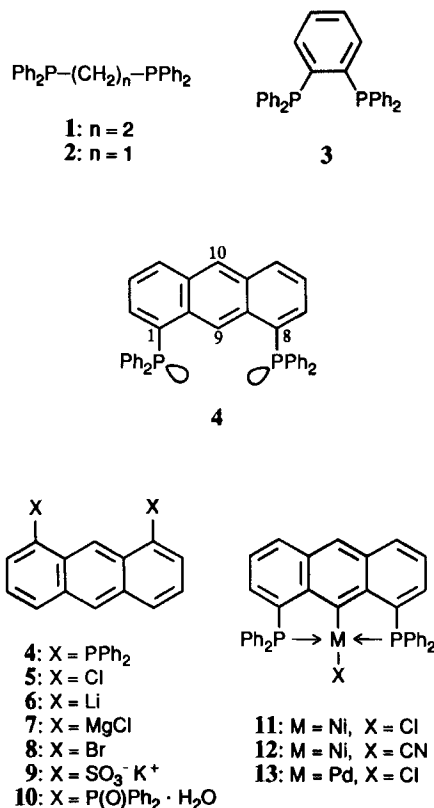
palladium complex **13**, the cyclometallated structure was proved by X-ray structure analysis. Treatment with aqueous potassium cyanide did not remove nickel from **11**, but converted **11** into **12** by substitution of chloride with cyanide, demonstrating the high stability of these cyclometallated chelate complexes.

Generally, bidentate phosphine ligands such as 1,2-bis(diphenylphosphino)ethane (**1**) or 1,2-bis(diphenylphosphino)benzene (**3**) coordinate metals to form preferably monometallic chelate complexes. If both phosphorus centres have mutual geometries unfavourable for the formation of monometallic chelate complexes, bimetallic complexes can also be obtained. For example, in the case of 1,2-bis(diphenylphosphino)methane (**2**) a monometallic chelate complex (involving the formation of a four-membered ring) is disfavoured, so that under certain conditions the bidentate ligand coordinates two metals²⁾. Another approach to form bimetallic complexes is the synthesis of bidentate phosphines in which rigid carbon skeletons are used to arrange two phosphorus centres at distances too long to coordinate simultaneously one metal nucleus, but short enough to bring two coordinated metals in close proximity. Such homo- or heterobinuclear metal complexes might bear interesting features and new potentials, especially with respect to catalytic processes³⁾.

In pursuing this concept we have synthesized 1,8-bis(diphenylphosphino)anthracene (**4**) and studied in preliminary experiments its behaviour as a ligand in metal complexation. Thereby monometallic nickel(II) and palladium(II) chelate complexes of **4** have been obtained, the formation of which has not been expected at first sight. While the intramolecular phosphorus–phosphorus distance of about 5 Å still is reasonable for chelate formation, the phosphorus valence angle and especially the steric requirements of the anthracene 9-hydrogen are unfavourable. However, if simultaneously with coordination to both phosphorus centres the metal is inserted into the C–H bond in anthracene 9-position, monometallic cyclometallated chelate complexes become feasible⁴⁾.

The synthesis of **4** has first been attempted starting from 1,8-dichloroanthracene⁵⁾ (**5**). However, it has not been possible to convert **5** by twofold metallation into either the dilithium compound **6** or the di-Grignard compound **7** from both of which **4** should have been accessible by the successive reaction with chlorodiphenylphosphine. The reaction of **5** with lithium diphenylphosphide (Ph_2PLi)⁶⁾ has given **4** only in yields below 2%. Anticipating higher reactivity, 1,8-dibromoanthracene (**8**, m. p. 162–165°C) has been synthesized from dipotassium 9,10-anthraquinone-1,8-disulfonate⁷⁾ by reaction with bromine in water (260°C, 48 h, 70% yield)⁸⁾ and subsequent reduction of the 1,8-dibromo-9,10-anthraquinone with aluminium cyclohexoxide⁹⁾ (72 h reflux in cyclohexanol, 77% yield). However,

8 could not be converted into **4** in reasonable yields either. Finally, by the use of the method of Zorn, Schindlbauer and Hagen¹⁰⁾, **4** has been obtained by reaction of anhydrous dipotassium 1,8-anthracenedisulfonate¹¹⁾ (**9**) with two equivalents of potassium diphenylphosphide (Ph_2PK)¹²⁾ in diethylene glycol diethyl ether for 20 h at 180°C. After chromatography (silica gel, cyclohexane/toluene), **4** has been isolated as a light yellow powder (33%, m. p. 233–235°C). For further characterization **4** has been oxidized by 30% aqueous hydrogen peroxide in boiling ethanol to give the colourless 1,8-(diphenylphosphoryl)anthracene (**10**) as the dihydrate (57%, m. p. > 320°C).



In the $^1\text{H-NMR}$ spectrum (CD_2Cl_2 , 200 MHz) of **4** the signals of the anthracene 9,10-H are widely separated ($\delta = 9.71$ and 8.49). The assignment of the lower-field signal to 9-H located between the two phosphorus groups is based on the chemical shift differing considerably from the usual range of the anthracene 9,10-H and the abnormally large coupling to phosphorus ($J_{\text{PH}} = 5.1$ Hz). In the most stable conformation enforced by the bulk of the phenyl substituents, the phosphorus lone pairs are oriented towards 9-H, thus causing a strong down-field shift and enabling "through space coupling"¹³. In the $^1\text{H-NMR}$ spectrum (CDCl_3 , 200 MHz) of the phosphine oxide **10**, on the other hand, the signals of the anthracene 9,10-H happen to coincide at $\delta = 9.19$ (s, br.), and the large phosphorus coupling of 9-H is not observed.

As the complexation behaviour of the bidentate phosphine **4** has so far been studied, two generally different types of metal complexes are observed: Cyclometallated chelate complexes **11** and **13** are formed with nickel(II) and palladium(II) chloride, respectively, whereas silver(I) and gold(I) salts are complexed exclusively to phosphorus without concomitant cyclometallation forming monometallic chelate and bimetallic complexes, respectively¹⁴. 1,8-Bis(diphenylphosphino)-9-anthrylnickel(II) chloride [**11**, yellow microcrystals, m. p. $> 260^\circ\text{C}$ (dec.), 77% yield after chromatography on silica gel with toluene/cyclohexane] has been obtained by heating a mixture (1:1:1) of **4**, $\text{NiCl}_2 \times 6 \text{H}_2\text{O}$, and diisopropylethylamine¹⁵ in ethylene glycol monomethyl ether at reflux for 45 min. The mass spectrum and especially the $^1\text{H-NMR}$ spectrum, lacking a signal for the anthracene 9-H, point to a cyclometallated chelate structure. This is further supported by the extreme stability of the metal complex: Treatment with aqueous potassium cyanide does not remove the nickel from **11**, but results in a partial exchange of chloride by cyanide and formation of a mixture of **11** and **12**^{16,17}.

1,8-Bis(diphenylphosphino)-9-anthrylpalladium(II) chloride (**13**, yellow-orange crystals, m. p. $> 320^\circ\text{C}$, 73% yield) has been formed by heating a mixture (1:1) of **4** and bis(benzonitrile)palladium(II) chloride in ethylene glycol monomethyl ether at reflux for 2 h. In this case the cyclometallated chelate structure has been established by X-ray structure analysis (Figure 1, a, b).

In the square-planar complex the distance between the anthracene carbon C-9 and palladium is 2.010(5) Å which is within the range usually found for $\text{C}_{\text{aryl}}-\text{Pd}$ σ -bonds¹⁸. The two bonds between palladium and the two phosphorus atoms [$\text{Pd}-\text{P}1$:

2.291(1); $\text{Pd}-\text{P}2$: 2.283(1) Å] are not completely collinear, but form an angle $\text{P}1-\text{Pd}-\text{P}2$ of $166.2(1)^\circ$. The valence angles at the carbon centres C-1,8 [$\text{C}11-\text{C}1-\text{P}1$: $112.8(4)^\circ$; $\text{C}14-\text{C}8-\text{P}2$: $112.4(3)^\circ$] and at both phosphorus centres [$\text{C}1-\text{P}1-\text{Pd}$: $102.3(2)^\circ$; $\text{C}8-\text{P}2-\text{Pd}$: $103.0(2)^\circ$] are diminished by about 8 and 6°, respectively. Possibly due to the ring strain within the five-membered rings, the anthracene unit is slightly distorted as shown by an angle of 4.1° between the planes $\text{C}1-\text{C}2-\text{C}3-\text{C}4-\text{C}12-\text{C}11$ and $\text{C}5-\text{C}6-\text{C}7-\text{C}8-\text{C}14-\text{C}13$.

In these cyclometallated chelate complexes of **4** the metal centre appears to be essentially unhindered only from the side opposite to the anthracene moiety and should be accessible to reagents and substrates from this side. The rotating phenyl substituents at the phosphorus centres should impede the access from the top and the bottom side. If the phenyl groups bonded on the different phosphorus centres have the face-to-face conformation as shown by the solid state structure (lower pair of phenyl groups in Figure 1, b), they leave a gap of about 3 Å possibly enabling small ligands such as hydride or carbon monoxide still to be coordinated to a suitable octahedral metal centre. The very strong metal bonding of **4** might be of interest for the development of catalysts. Like the anthracene unit in **4**, other polycyclic arenes or heteroarenes might also be useful as rigid backbones for bidentate phosphines²⁰.

Experimental

All operations were carried out under an atmosphere of dry argon. Solvents were dried, distilled and stored under argon. Elemental analyses were carried out by the microanalytical laboratory Dornis & Kolbe, D-4330 Mülheim/Ruhr. — $^1\text{H NMR}$: Bruker WP 80 and AM 200, tetramethylsilane as internal standard. — $^{31}\text{P NMR}$: Bruker WP 80 and AM 200 (81 MHz), phosphoric acid as external standard. — IR: Nicolet 7199 FT spectrometer, pressed potassium bromide discs. — MS: Finnigan MAT 311 A, EI at 70 eV. — GC/MS: Hewlett-Packard HP 5890 A with HP 5970 MSD. — GC: Hewlett-Packard HP 5890 A, Packard 427, Siemens Sichromat, capillary columns coated with OV-1, PS-240, PS-428, SE-54 or CW-20, respectively²¹.

1,8-Dibromoanthracene (**8**): To a suspension of 1.83 g (5.0 mmol) of 1,8-Dibromo-9,10-anthraquinone (prepared from dipotassium 9,10-anthraquinone-1,8-disulfonate⁷) by reaction with bromine in

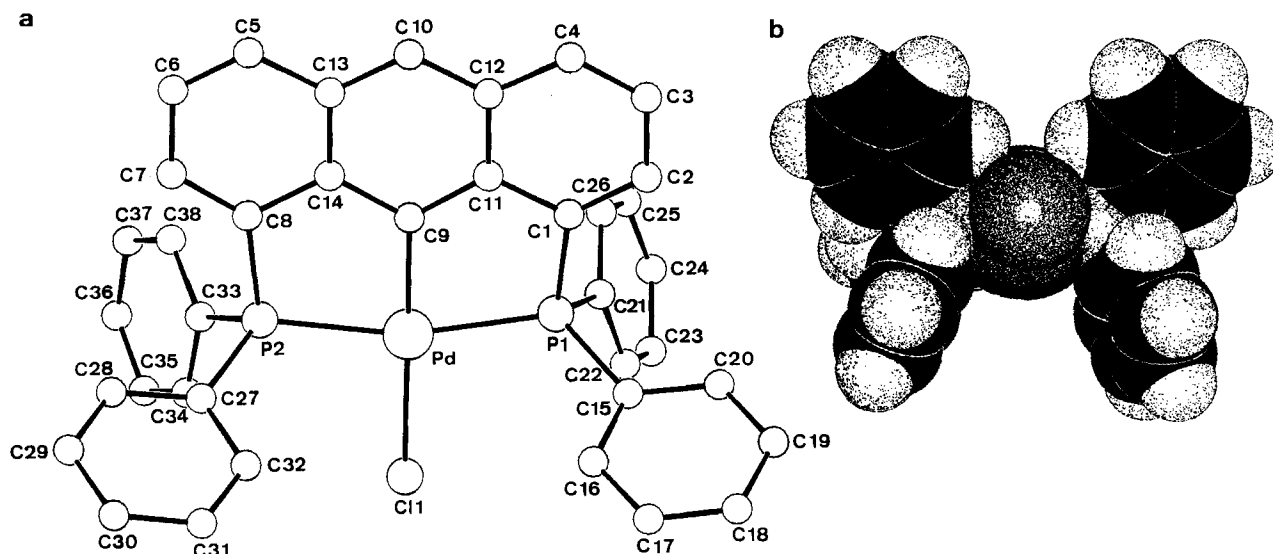


Figure 1. Molecular structure of 1,8-bis(diphenylphosphino)-9-anthrylpalladium(II) chloride (**13**) (chloroform molecule omitted); a: top view; b: front view on chloro side (space filling Schakal, E. Keller, University of Freiburg)

water, 260 °C, 48 h, 70% yield⁸⁾ in 10 ml of cyclohexanol, 18 ml of aluminium cyclohexoxide in cyclohexanol (1.85 M, 33.3 mmol)⁹⁾ was added, and the mixture was heated at reflux for 72 h. The hot solution was poured into water, and worked up by extraction with toluene, chromatography on silica gel with cyclohexane and crystallization from ethanol yielded 1.29 g (77%) **8**, light-yellow powder with m.p. 162–165 °C. — ¹H NMR (CDCl₃, 200 MHz): δ = 9.08 (s, 1H, anthracene 9-H) 8.28 (s, 1H, 10-H), 7.87, 7.76, 7.25 (AMX with J_{AX} = 8.0, J_{MX} = 8.6, J_{AM} = 0.9 Hz; each 2 H for 2,7-H, 4,5-H and 3,6-H). — MS (70 eV): m/z (%) = 339 (7), 338 (48), 337 (14), 336 (100), 335 (8), 334 (49) [M⁺ with ⁷⁹Br, isotopic pattern as calcd. for 2 Br], 257 (14), 255 (13), 176 (54), 88 (19).

C₁₄H₈Br₂ (336.03) Calcd. C 50.04 H 2.40 Br 47.56
Found C 49.65 H 2.38 Br 47.75

1,8-Bis(diphenylphosphino)anthracene (4): Dipotassium 1,8-anthracenedisulfonate (**9**), obtained as dihydrate from dipotassium 9,10-anthraquinone-1,8-disulfonate⁷⁾ by zinc dust reduction in aqueous sodium hydroxide solution with 86% yield¹¹⁾, was dried at 120 °C for several days in high vacuum until in the IR spectrum the OH band had been disappeared. A solution of potassium diphenylphosphide (Ph₂PK) was prepared by addition of 27.6 g (124.7 mmol) of chlorodiphenylphosphine within 1 h to a dispersion of 9.8 g (250.6 mmol) of potassium in 170 ml of diethylene glycol diethyl ether at 120–125 °C and stirring the mixture at this temp. for 2 h^{10,12)}. To this brown-red solution 25.0 g (60.3 mmol) of anhydrous **9** was added and the mixture stirred at 180 °C for 20 h. After hydrolysis with iced water, the organic layer was separated and dried with sodium sulfate. The solvent was removed in vacuum and the residue purified by chromatography on silica gel with cyclohexane/toluene (10:1 to 1:1) to yield 11.0 g (33%) of **4** as a light-yellow powder, m.p. 233–235 °C. — ¹H NMR (CD₂Cl₂, 200 MHz): δ = 9.71 (t, J_{PH} = 5.1 Hz, 1H, anthracene 9-H), 8.49 (s, br., 1H, 10-H), 8.02, 7.35, 7.03 (AMX with J_{AX} = 8.7, J_{MX} = 7.4, J_{AM} = 1.2 Hz; A and X further splitted by J_{PH} = 1.2 Hz and J_{PH} = 1.3 Hz, respectively; each 2H for 2,7-H, 4,5-H and 3,6-H), 7.22–7.03 (m, 20H, phenyl H). — ³¹P NMR (CD₂Cl₂, 81 MHz): δ = –14.2 (s). — MS (70 eV): m/z (%) = 547 (42), 546 (100) [M⁺], 545 (14), 359 (19), 283 (12), 281 (18), 183 (11).

C₃₈H₂₈P₂ (546.59) Calcd. C 83.50 H 5.16
Found C 83.88 H 4.97

1,8-Bis(diphenylphosphoryl)anthracene (10): To a solution of 0.31 g (5.7 mmol) of **4** in 80 ml of ethanol 2 ml of aqueous hydrogen peroxide (30%) was added and the mixture heated at reflux for 30 min. Hydrolysis, extraction with dichloromethane, evaporation of the solvent and recrystallization from dichloromethane/diethyl ether yielded 0.20 g (57%) of colourless **10** as dihydrate, m.p. > 320 °C. — ¹H NMR (CDCl₃, 200 MHz): δ = 9.19 (s, br., 2H, anthracene 9,10-H), 7.99–7.96 (m, 2H), 7.67–7.55 (m, 8H), 7.52–7.29 (m, 12H), 7.25–7.10 (m, 4H), 2.05 (s, br., 4H, H₂O). — ³¹P NMR (CDCl₃, 81 MHz): δ = +33.3 (s). — IR (KBr): 3460 cm⁻¹ (br., H₂O), 1175 (s, P=O). — MS (70 eV): m/z (%) = 579 (37), 578 (100) [M⁺], 577 (72), 201 (51), 183 (17), 77 (18).

C₃₈H₂₈O₂P₂ × 2 H₂O (614.62) Calcd. C 74.26 H 5.25 P 10.08
Found C 73.65 H 5.03 P 9.69

1,8-Bis(diphenylphosphino)-9-anthrylnickel(II) Chloride (11): 145.0 mg (0.61 mmol) of nickel(II) chloride hexahydrate was added to a solution of 333.1 mg (0.61 mmol) of **4** in 100 ml of ethylene glycol monomethyl ether at 100 °C. After stirring the mixture at 100 °C for 10 min, 0.11 ml (0.61 mmol) of diisopropylethylamine was added and the mixture heated at reflux for a further 45 min. The yellow-orange solution was concentrated in vacuum to 30 ml and the precipitated solid isolated by filtration and washed with

ethanol. According to the ³¹P-NMR spectrum this solid consisted of **4** and **11**. After chromatography on silica gel with cyclohexane/toluene and crystallization from ethanol/chloroform 300 mg (77%) of **11** was obtained in yellow microcrystals, m.p. > 260 °C (dec.). — ¹H NMR ([D₈]toluene, 200 MHz): δ = 7.95 (t, J = 2.4 Hz, 1H, anthracene 10-H), 7.89–7.75 (m, 10H, 2,7-H and phenyl H), 7.40 (m, 2H, 4,5-H), 7.21 (dddd, J_{HH} = 8.1 Hz, J_{HH} = 6.8 Hz, J_{HH} ≈ J_{PH} ≈ 1.35 Hz, 2H, 3,6-H), 7.13–7.00 (m, 12H, phenyl H). — ³¹P NMR ([D₈]toluene, 81 MHz): δ = +42.1 (s). — MS (70 eV): m/z (%) = 644 (4), 643 (8), 642 (23), 641 (31), 640 (79), 639 (41), 638 (100) [M⁺ with ⁵⁸Ni and ³⁵Cl], 605 (2), 604 (2), 603 (4) [(M⁺ with ⁵⁸Ni) – Cl], 320 (13), 319 (16), 281 (38); for M⁺ and (M⁺ – Cl) isotopic pattern as calcd.

C₃₈H₂₇ClNiP₂ (639.72)

A satisfactory elemental analysis could not be obtained.

Calcd. 638.06304 Found 638.06342 ± 0.00221 (MS)

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters [Å²] with standard deviations in parentheses^{a)}

Atom	x	y	z	U _{eq}
Pd	0.1313(1)	0.2015(1)	0.4668(1)	0.036(1)
CL(1)	0.1712(1)	0.2963(1)	0.3653(1)	0.064(1)
P(1)	0.2535(1)	0.1177(1)	0.4392(1)	0.040(1)
P(2)	0.0064(1)	0.2664(1)	0.5237(1)	0.037(1)
C(1)	0.2195(4)	0.0368(3)	0.4999(3)	0.039(3)
C(2)	0.2612(4)	-0.0324(3)	0.4977(4)	0.049(3)
C(3)	0.2251(5)	-0.0916(3)	0.5474(4)	0.056(4)
C(4)	0.1502(4)	-0.0799(3)	0.5997(4)	0.052(4)
C(5)	-0.0967(4)	0.0885(3)	0.7135(4)	0.050(4)
C(6)	-0.1400(4)	0.1550(4)	0.7138(4)	0.056(4)
C(7)	-0.1124(4)	0.2130(3)	0.6570(4)	0.049(3)
C(8)	-0.0385(4)	0.2017(3)	0.6022(3)	0.039(3)
C(9)	0.0921(3)	0.1207(3)	0.5489(3)	0.034(3)
C(10)	0.0269(4)	0.0048(3)	0.6579(4)	0.046(3)
C(11)	0.1384(3)	0.0503(3)	0.5514(3)	0.035(3)
C(12)	0.1048(4)	-0.0091(3)	0.6047(3)	0.041(3)
C(13)	-0.0189(4)	0.0735(3)	0.6585(3)	0.039(3)
C(14)	0.0123(3)	0.1318(3)	0.6032(3)	0.034(3)
C(15)	0.2599(4)	0.0899(3)	0.3200(4)	0.045(3)
C(16)	0.1842(4)	0.1128(4)	0.2483(4)	0.054(4)
C(17)	0.1837(5)	0.0864(4)	0.1588(4)	0.071(5)
C(18)	0.2565(6)	0.0381(4)	0.1408(4)	0.074(5)
C(19)	0.3342(6)	0.0154(4)	0.2111(5)	0.077(5)
C(20)	0.3372(5)	0.0420(4)	0.3013(4)	0.063(4)
C(21)	0.3859(4)	0.1419(3)	0.4907(4)	0.046(3)
C(22)	0.4436(5)	0.1846(4)	0.4401(5)	0.066(4)
C(23)	0.5401(6)	0.2092(5)	0.4816(7)	0.090(6)
C(24)	0.5795(5)	0.1916(5)	0.5729(8)	0.094(7)
C(25)	0.5228(6)	0.1507(5)	0.6223(6)	0.088(6)
C(26)	0.4259(5)	0.1238(4)	0.5820(4)	0.065(4)
C(27)	-0.1063(4)	0.2959(3)	0.4403(3)	0.040(3)
C(28)	-0.1871(4)	0.3337(3)	0.4701(4)	0.051(3)
C(29)	-0.2729(5)	0.3540(4)	0.4073(5)	0.065(4)
C(30)	-0.2797(5)	0.3379(4)	0.3149(5)	0.075(5)
C(31)	-0.2012(6)	0.3011(4)	0.2839(4)	0.074(5)
C(32)	-0.1142(5)	0.2807(4)	0.3461(4)	0.059(4)
C(33)	0.0494(4)	0.3480(3)	0.5910(4)	0.044(3)
C(34)	0.0722(5)	0.4107(4)	0.5451(5)	0.069(5)
C(35)	0.1105(6)	0.4736(4)	0.5970(7)	0.087(6)
C(36)	0.1257(6)	0.4728(5)	0.6908(7)	0.088(6)
C(37)	0.1025(6)	0.4125(5)	0.7375(5)	0.088(6)
C(38)	0.0662(5)	0.3489(4)	0.6893(4)	0.063(4)
CL(2)	0.4329(3)	0.4012(3)	0.4713(3)	0.191(4)
CL(3)	0.3922(4)	0.3420(4)	0.6489(3)	0.249(6)
CL(4)	0.3856(8)	0.4564(8)	0.5911(8)	0.53(2)
C(39)	0.358(1)	0.3586(8)	0.5417(8)	0.16(1)

$$^a) U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$$

1,8-Bis(diphenylphosphino)-9-anthrylpalladium(II) Chloride (13): A suspension of 262.9 mg (0.48 mmol) of **4** and 184.3 mg (0.48 mmol) of bis(benzonitrile)palladium(II) chloride in 10 ml of ethylene glycol monomethyl ether was heated at reflux for 2 h. After cooling to room temp. the yellow precipitate was filtered off, washed twice with 3-ml portions of ethylene glycol monomethyl ether and dried in high vacuum to yield 240.1 mg (73%) of **13** as yellow-orange crystals, m. p. > 320°C. — ¹H NMR (CD₂Cl₂, 200 MHz): δ = 8.29 (t, *J* = 2.7 Hz, 1H, anthracene 10-H), 8.08 (m, 2H, 2,7-H), 7.88–7.77 (m, 8H, phenyl H), 7.70 (m, 2H, 4,5-H), 7.51 (dddd, *J*_{HH} = 8.3 Hz, *J*_{HH} = 7.0 Hz, *J*_{HH} ≈ *J*_{PH} ≈ 1.2 Hz, 2H, 3,6-H), 7.43–7.29 (m, 12H, phenyl H). — ³¹P NMR (CD₂Cl₂, 81 MHz): δ = +43.5 (s). — MS (70 eV): *m/z* (%) = 693 (3), 692 (10), 691 (16), 690 (42), 689 (29), 688 (75), 687 (40), 686 (75) [M⁺ with ¹⁰⁶Pd and ³⁵Cl], 685 (50), 684 (21), 656 (9), 655 (25), 654 (21), 653 (54), 652 (26), 651 (71) [(M⁺ with ¹⁰⁶Pd) – Cl], 650 (50), 649 (26), 613 (9), 612 (5), 611 (16), 610 (8), 609 (16) [(M⁺ with ¹⁰⁶Pd and ³⁵Cl) – Ph], 608 (11), 607 (5), 345 (13), 344 (22), 343 (22), 313 (31), 312 (21), 283 (37), 382 (24), 281 (100), 183 (13); for M⁺, (M⁺ – Cl) and (M⁺ – Ph) isotopic pattern as calcd.

C₃₈H₂₇ClP₂Pd (687.45)

Calcd. C 66.39 H 3.96 Cl 5.16 P 9.01 Pd 15.48

Found C 65.81 H 3.91 Cl 5.29 P 9.12 Pd 15.84

X-ray Structure Analysis of 13: Suitable crystals were obtained by slowly evaporating a solution of **13** in chloroform. C₃₈H₂₇ClP₂Pd × CHCl₃, crystal size 0.18 × 0.40 × 0.43 mm, mol. mass 806.5, *a* = 13.101(1), *b* = 18.112(2), *c* = 14.508(2) Å, β = 99.97(1)°, *V* = 3390.4 Å³, *d*_{calcd.} = 1.58 g cm⁻³, μ = 9.77 cm⁻¹, *Z* = 4, space group *P2₁/n*, λ = 0.71069 Å, Nonius CAD4 diffractometer, 8248 measured reflections (±*h*, +*k*, +*l*), (sinθ/λ)_{max} = 0.65, 7704 independent and 5934 observed reflections, 415 refined parameters, *R* = 0.055, *R_w* = 0.065, *Q*_{max} = 1.52 e Å⁻³. The chloroform molecules are disordered and not bonded to **13**, absorption correction did not improve the disorder. The atomic coordinates and thermal parameters are listed in Table 1²².

CAS Registry Numbers

4: 131276-25-0 / **8:** 131276-24-9 / **9:** 66601-73-8 / **10:** 131276-23-8 / **11:** 131276-26-1 / **13:** 131276-28-3 / Ph₂PK: 15475-27-1 / dipotassium 9,10-anthraquinone-1,8-disulfonate: 14938-42-2 / chlorodiphenylphosphine: 1079-66-9 / nickel(II) chloride: 7718-54-9 / bis(benzonitrile)palladium(II) chloride: 14220-64-5 / 1,8-dibromo-9,10-anthraquinone: 38313-16-5 / aluminium cyclohexoxide: 1971-69-3

¹ This work is part of the doctoral thesis of D. Jakubik, University of Düsseldorf, 1990.

² See e.g.: R. J. Puddephatt, *J. Chem. Soc. Rev.* **12** (1983) 99. — D. M. Hoffman, R. Hoffmann, *Inorg. Chem.* **20** (1981) 3543. — A. Miedaner, D. L. DuBois, *Inorg. Chem.* **27** (1988) 2479.

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¹⁴ The silver(I) and gold(I) complexes of **4** formed with silver triflate and gold(I) chloride will be described in a forthcoming communication.

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¹⁶ **12** was identified in the mixture spectroscopically: MS (70 eV): *m/z* (%) = 633 (7), 632 (17), 631 (43), 630 (41), 629 (100) [M⁺ with ⁵⁸Ni], 605 (1), 604 (1.6), 603 (2.2) [(M⁺ with ⁵⁸Ni) – CN], 602 (1.4), 494 (30), 281 (64); for M⁺ and (M⁺ – CN) isotopic pattern as calcd. — IR (KBr): 2110 cm⁻¹ (CN).

¹⁷ For the tetracyanonickelate(II) complex the cumulative dissociation constant *K_D* = (Ni²⁺)(CN⁻)⁴/Ni(CN)₄²⁻ has been determined to be (1.0 ± 0.2) × 10⁻³¹ at 25°C; H. Freund, C. R. Schneider, *J. Am. Chem. Soc.* **81** (1959) 4780.

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²² Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54914, the names of the authors, and the journal citation.