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Monodentate and Bridging Coordination of 3,3′-Annelated 2,2′-Bipyridines in Zerovalent Palladium- and Platinum-*p*-quinone Complexes

René A. Klein[a], Peter Witte[a], Ruud van Belzen[a], Jan Fraanje[b], Kees Goubitz[b], Milco Numan[b], Henk Schenk[b], Jan M. Ernsting[a], and Cornelis J. Elsevier*[a]

J. H. van′t Hoff Research Institute[a], Universiteit van Amsterdam,
Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands
Fax: (internat.) +31(0)20/5256456
E-mail: else4@anorg.chem.uva.nl

Amsterdam Institute of Molecular Studies[b], Universiteit van Amsterdam,
Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands

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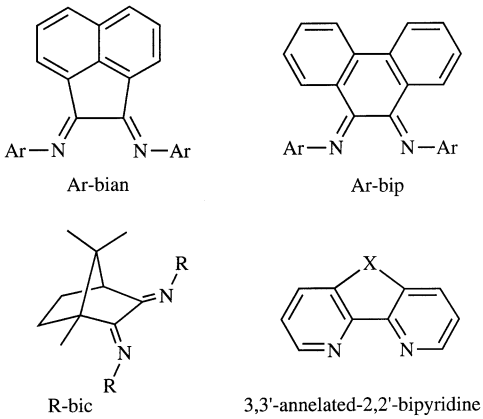
Compounds of the type M(N∩N-κ*N*)(nq)$_2$ and M$_2$(μ^2-N∩N)-(μ^2-pbq)$_2$, in which nq = 1,4-naphthoquinone, pbq = 1,4-benzoquinone, and N∩N is a monodentate or bridging ligand of the α-diimine type, were obtained from reactions of Pd(dba)$_2$ in toluene with the 3,3′-annelated-2,2′-bipyridines: 4,5-diazafluoren-9-one (dafo) and 4,5-diazafluorene (dafe) in the presence of the appropriate *p*-quinone. In the corresponding reactions with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′-bipyrimidine (bpym), *N*,*N*′-dicyclohexyl-1,4-diaza-1,3-butadiene (chex-dab), bis[*N*-(*o*,*o*′-diisopropyl)phenylimino]acenaphthene (*o*,*o*′-*i*Pr$_2$-bian) and 5,6-dihydro-1,10-phenanthroline (dh-phen) only complexes of the type M(N∩N-κ^2*N*)(Q) were formed (Q = nq, pbq). The structures of the complexes have been established by NMR in solution and by X-ray diffraction in the solid state; crystal structures of Pd(bpy-κ^2*N*)(η^2-pbq) (**1**) Pd(dafo-κ*N*)(η^2-nq)$_2$ (**14**) and Pd$_2$(μ^2-dafo)(μ^2,η^2:η^2-pbq)$_2$ (**16**) have been determined. Of the ligands, dafo and dafe are the only ones apt to form complexes containing a monodentate or bridging N∩N ligand. This behaviour is ascribed to the geometrical constraints of dafo and dafe; the annelation by one carbon atom at the 3,3′-positions in these ligands causes an increase in bite angle from approximately 77° to 82°.

Introduction

The chemistry of complexes containing an alkene coordinated to a low-valent metal from the platinum group has received considerable attention and studies have been particularly aimed at trigonal planar zerovalent platinum and nickel complexes of general formula ML$_2$(alkene) where L is a phosphane[1][2][3]. Zerovalent palladium complexes containing nitrogen ligands have received relatively little attention.[4][5][6] We have previously reported about compounds consisting of organopalladium or -platinum fragments (where the metal has the formal oxidation state II or IV) and a rigid bidentate nitrogen ligand (RBN), such as bis(*N*-arylimino)acenaphthene (Ar-bian)[7], bis(*N*-phenylimino)camphane (Ar-bic), bis(*N*-arylimino)phenanthrene (Ar-bip)[8], see Figure 1, as well as those containing zerovalent palladium and an electron-deficient alkene[6].

These and similar compounds are versatile catalysts in e.g., catalytic (multicomponent) C-C coupling reactions[9][10][11], in homogeneous catalyzed hydrogenation of alkenes[12] and as models for copolymerization and as active catalysts in polymerizations of alkenes[13][14]. The rigid bidentate ligands employed sofar by us have bite-angles of about 77°.

Figure 1. Rigid bidentate nitrogen ligands



In many cases, bidentate ligands may dissociate one ligating atom (if only temporarily) during a reaction sequence, or undergo elongation of one of the metal-to-ligand bonds, as has been shown for an increasing number of cases, not only those involving hemi-labile ligands[15]. Monodentate coordination has e.g. been observed for phenanthrolines[16]

[◇] For part 13, see ref.[18], part 12, see ref.[11]. Netherlands Institute for Research in Catalysis (NIOK) publication uva 98-3-01.

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and for an Ar-bian ligand in the case of an(η^3-allyl)Pd^{II} compound[17], but not for complexes of Pd^0. Despite these observations, there is a clear tendency of the Ar-bian and similar rigid ligands to remain bidentate coordinated to the metal centre, which is partly caused by the favourable bite-angle of about 77°.

It was anticipated that a slight increase of the bite-angle, while maintaining rigidity, would lead to reduced overlap between relevant metal and ligand orbitals and hence to an enhanced aptitude for dissociation of one of the donor atoms. To this end we have turned to members of the series of 3,3′-annelated-2,2′-bipyridines, for which the bite angle as well as the planarity of the ligand system varies with the number of methylene groups in the bridge[18] especially 4,5-diazafluoren-9-one (dafo)[19] and 4,5-diazafluorene (dafe)[20], see Figures 2 and 3.

Figure 2. Ligands and abbreviations

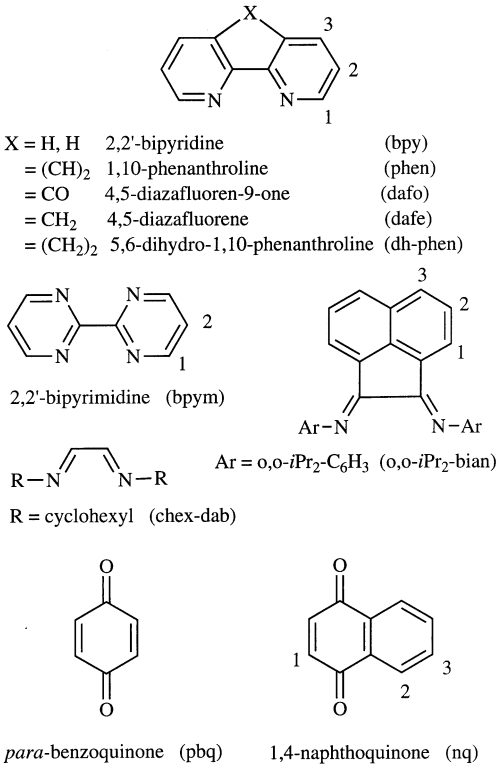
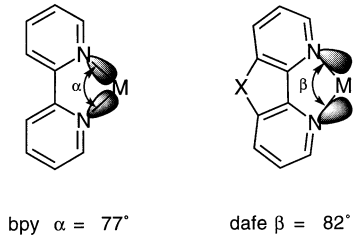


Figure 3. Decreasing orbital overlap between the metal atom (M = Pd, Pt) and a bidentate coordinating α-diimine ligand going from bipyridine (α = 77°) to dafo (X = CO) and dafe (X = CH2; β = 82°)



For dafo and dafe the bite-angle is 82°[18]. Consequently, one may expect that the altered lone-pair orientation on the nitrogen donor atoms of dafo and dafe, as illustrated in Figure 3, would facilitate the monodentate or bridging coordination mode for these ligands. In order to substantiate our expectations, we have decided to undertake a study of coordination compounds of zero-valent Pd and Pt containing the bidentate nitrogen ligands mentioned and suitable alkenes. For comparison, we employed a series of other rigid and flexible α-diimine ligands, such as 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-bipyrimidine, 1,4-diaza-1,3-butadiene, and Ar-bian (Figure 2). In keeping with previous studies[21][22][23][24][25][26][27][28][29][30][31][32][33][34][35][36][37], stabilization of the zerovalent metal center by employing the strong π-acceptor *p*-quinone (Q) ligands *para*-benzoquinone (pbq) and 1,4-naphthoquinone (nq) was anticipated. Since *p*-quinones are potentially bidentate ligands, the ML_2Q complexes could be tetrahedral although it is well known that Pd^0 shows a tendency to be trigonal planar[38]. Furthermore because of the bisalkenic function of the *p*-quinones, it was foreseen that these might also support the formation of dinuclear complexes with bridging ligands[25][31][32][34].

In this paper the propensity of the 3,3′-annelated-2,2′-bipyridine ligands to stabilize compounds in which the bisnitrogen ligand coordinates in a monodentate way, i.e., $M(N\cap N\text{-}\kappa N)(\eta^2\text{-nq})_2$, or in which both the bisnitrogen ligand as well as *p*-benzoquinone are bridging between two metal centers, i.e., $M_2(\mu^2\text{-}N\cap N)(\mu^2,\eta^2\text{:}\eta^2\text{-pbq})_2$, is demonstrated. The structural and bonding features of these unique complexes have been elucidated, both in the solid state and in solution.

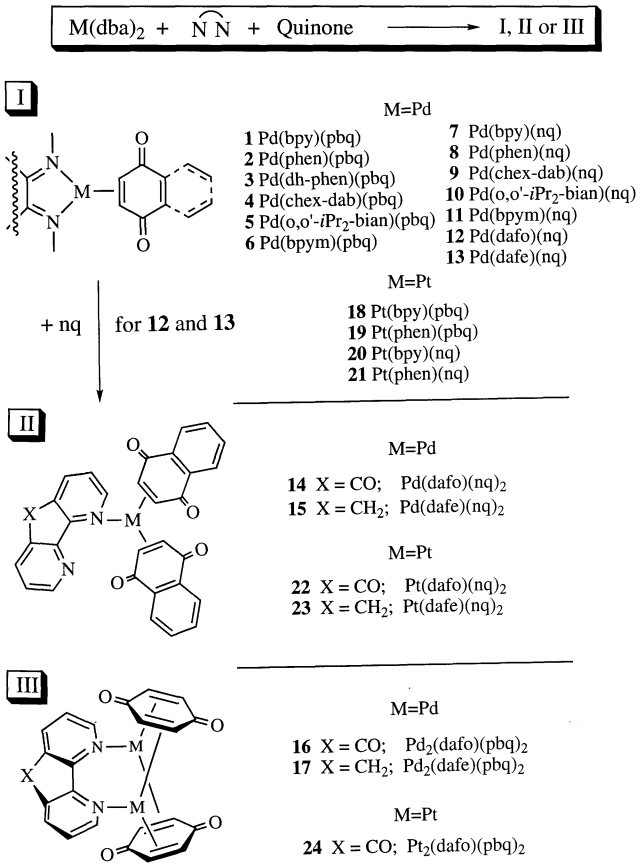
Results and Discussion

Synthesis of Zerovalent Palladium and Platinum Complexes (1−24)

At first, attempts were made to synthesize zerovalent Pd(N∩N)(alkene) complexes with electron poor alkenes such as dimethylfumarate, fumaronitrile or maleic anhydride. Unfortunately, for the bisnitrogen ligands, dafo, dafe or dh-phen (Figure 2), no isolable zerovalent palladium complexes could be obtained with any of these alkenes. However, employing the more electron-accepting *p*-quinones, relatively stable zerovalent palladium and platinum complexes have been obtained (Scheme 1).

Independent of the relative amount of starting materials, i.e. $Pd(dba)_2$, alkene and bidentate nitrogen ligand (Figure 2), zerovalent palladium complexes **1**−**11** with the general formula Pd(N∩N)(alkene) were formed [Scheme 1, type I; N∩N= bpy, phen, dh-phen, chex-DAB, *o,o′*-iPr_2-bian or bpym, and alkene = 1,4-benzoquinone (pbq) or 1,4-naphthoquinone (nq)]. Compounds **1**, **2**, **7**, and **8** have been reported previously[27]. The analytical data together with the crystal structure of Pd(bpy)(η^2-pbq) (**1**)[39] confirmed the 1:1:1 ratio of the metal, bisnitrogen ligand and *p*-quinone. These complexes are well soluble and stable in polar solvents such as chloroform, dichloromethane and tetrahydrofuran. Complexes containing bpym, *o,o′*-iPr_2-bian, cyclohexyl-DAB are even slightly soluble in ether and therefore they had to be synthesized in a slightly different way.

Scheme 1. Synthesis of zerovalent palladium and platinum complexes. bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, chex-dab = N,N′-dicyclohexyl-1,4-diaza- 1,3-butadiene, *o,o′*-*i*Pr2-bian = bis{*N*-(*o,o′*-diisopropyl)-phenylimino}acenaphthene, bpym = 2,2′-bipyrimidine, dafo = 4,5-diazafluoren-9-one), dafe = 4,5-diazafluorene, dh-phen = 5,6-dihydro-1,10-phenanthroline; pbq = 1,4-benzoquinone, nq = 1,4-naphthoquinone.



The Pd(N∩N-κ^2*N*)(*p*-quinone) complexes (**12**, **13**) were obtained using dafe or dafo and nq in a ratio 1:1:1 with respect to the starting material Pd(dba)$_2$. When using two equivalents of nq with respect to the starting material Pd(dba)$_2$ in the presence of dafo or dafe, the reaction resulted in complexes with the formula Pd(N∩N-κ*N*)(η^2-nq)$_2$ (**14**, **15**), as appeared from the ^{1}H NMR, analytical data, and an X-ray crystal structure for **14** (Scheme 1, type II). In these complexes a feature *uniquely* observed for these ligands occurs: dafo and dafe coordinate in a *monodentate* fashion and both nq ligands are η^2-coordinated. These complexes could also be prepared by adding one equivalent of nq to the complexes Pd(N∩N-κ^2*N*)(η^2-nq) (**12**, **13**) by substitution of one nitrogen atom. The compounds are soluble in polar solvents, but not very stable, decomposition takes place even at low temperatures.

When dafo or dafe was employed in combination with pbq, instead of nq, in attempts to synthesize zerovalent palladium complexes of the types mentioned above, yet another type of complex was obtained. Analytical and ^{1}H-NMR data revealed that, independent of the applied stoichiometry, always a complex of type Pd$_2$(μ^2-N∩N)(μ^2,η^2:η^2-pbq)$_2$ (**16**, **17**) was formed (Scheme 1, type III). Their molecular structure was confirmed by a single-crystal X-ray structure determination for **16** (vide infra). When using substoichiometric amounts of dafo or dafe and pbq with respect to the palladium metal, again complexes **16** and **17** were formed and part of the Pd(dba)$_2$ was recovered. The structure of a related dinuclear zerovalent palladium compound containing a bridging DAB moiety, [Pd(dmfu)$_2$]$_2$-μ-DAB, (DAB = *t*BuN=CH−CH=N*t*Bu), has been postulated but not isolated[40]. The complexes **16** and **17** are poorly soluble in polar solvents, in which slow decomposition takes place.

Several platinum analogues (**18**−**24**) could be synthesized in a similar way starting from Pt(dba)$_2$ (Scheme 1), albeit that, due to the slower substitution at platinum compared to palladium, distinctly longer reaction times were required.

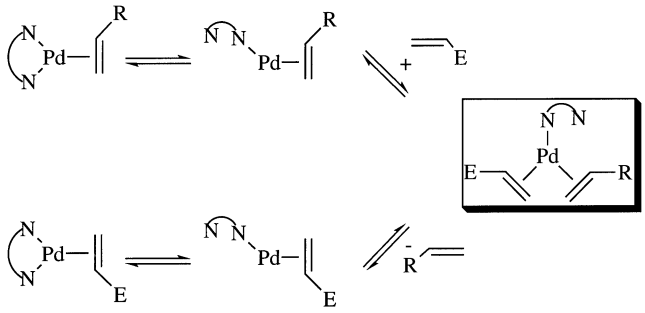
p-Quinone Substitution Reactions

In order to determine (i) the relative thermodynamic stability of the various complexes and (ii) the coordination behaviour of the respective N∩N-ligands in these cases, several *p*-quinone exchange reactions were carried out. The 1,4-naphthoquinone (nq) in the complex of type Pd(N∩N-κ^{2}N)(nq) (**7**−**11**) can be readily substituted for *p*-benzoquinone (pbq), adding one equivalent of the latter to these complexes yielded the Pd(N∩N−κ^2*N*)(pbq) analogues (**1**, **2**, **4**−**6**). Interestingly, when adding one equivalent of pbq to Pd(N∩N-κ^2*N*)(η^2-nq) (**12**, **13**), the novel bridged compounds Pd$_2$(μ^2-N∩N)(μ^2,η^2:η^2-pbq)$_2$ (**16**, **17**) were formed with the concomitant release of one molecule of bidentate nitrogen ligand and nq, instead of Pd(N∩N-κ*N*)(η^2-nq)(η^2-pbq). Adding an excess of nq to the Pd(N∩N-κ^2*N*)(η^2-nq) complexes (**7**−**11**) did not result in substitution of a nitrogen donor in these complexes, which would have resulted in the formation of complexes similar to Pd(N∩N−κ*N*)(η^2-nq)$_2$ (**14**, **15**). The formation of the latter type of complex is thus an exclusive property of the dafo and dafe within this series of bidentate nitrogen ligands. Adding one equivalent of pbq to the complex Pd(N∩N-κN)(η^2-nq)$_2$ (**14**, **15**) did not yield the mixed *p*-quinone complexes either; complete conversion to Pd$_2$(μ^2-N∩N)(μ^2,η^2:η^2-pbq)$_2$ (**16**, **17**) took place. Adding substoichiometric quantities of pbq to Pd(N∩N−κN)(η^2-nq)$_2$ (**14**, **15**) yielded only a mixture of Pd$_2$(μ^2-N∩N)(μ^2-pbq)$_2$ (**16**, **17**) and Pd(N∩N-κN)(η^2-nq)$_2$ (**14**, **15**), no mixed *p*-quinone complexes were observed. Adding nq to any of the complexes containing pbq did not result in substitution, the starting compounds were recovered. Hence, the complexes containing pbq are thermodynamically more stable than the complexes containing nq, which order is consistent with the relative electron-accepting properties of the *p*-quinones[35][35][37].

Alkene Substitution Reaction

The mechanism of alkene substitution in zerovalent palladium and platinum complexes has been described either by dissociative [via 14e Pd(N∩N-κ^2*N*)] or associative [via Pd(N∩N-κ^2*N*)(alkene)$_2$] pathways[6][41][42][43][44]. Clearly,

Scheme 2. Possible mechanism of alkene substitution in which the complexes **14**, **15**, **22**, and **23** are representative for the Pd(N∩N-κ*N*)(alkene)$_2$ intermediate



one of the donor atoms of the N∩N-ligand dafo or dafe can be non-coordinating, as has been unequivocally demonstrated by the isolation of the complexes **14**, **15**, **22**, and **23** and the X-ray crystal structure of **14**. These are 16-electron, Pd(N∩N-κ*N*)(η^2-alkene)$_2$ species. Hence, in addition to the mechanisms for alkene exchange mentioned above, the pathway as outlined in Scheme 2, in which dissociation of one of the N donor atoms of plays a key role, should be taken into account[45].

X-ray Crystal Structures of 1, 14, and 16

The molecular structures of **1, 14**, and **16** and the adopted numbering schemes are given in Figures 4−6. Selected bond distances and angles have been compiled in Tables 1 and 2. In all three complexes the palladium atom adopts a trigonal coordination geometry (taking the mid-point of the η^2-bond of the quinone as the point of attachment). In complex **1**, the palladium atom is bonded to two nitrogen atoms of the bpy ligand and one alkenic moiety of the *p*-quinone molecule. In complexes **14** and **16**, palladium is bonded to one nitrogen atom and to two alkenic moieties. In the latter complex, dafo bridges between two Pd^0 centers. In complexes **1** and **14** the *p*-quinone acts as a mono-, and in complex **16** as a bis-alkenic ligand.

The average Pd−N distances in **14** and **16** are comparable to those in several other Pd−α-diimine complexes, e.g. in PdCl(Me)(9,10-Me_2Phen)(ma)[46], PdCl(Me)(*o,o'*-*i*Pr_2-bian)[7], Pd(*o,o'*-*i*Pr_2-bian)(ma)[6] and in Pd(bpy)(dba)[47], but in **1** it is significantly shorter and similar to Pd(*p*-Tolbian)(ma)[48]. The average Pd−C distances are shorter than those in most other Pd(N∩N)(η^2-alkene) complexes, i.e. in PdCl(Me)(9,10-Me_2Phen)(ma)[46], Pd(bpy)(dba)[47], $Pd(dba)_3$[49], $Pd_2(dba)_3\cdot CH_2Cl_2$[50], $Pd_2(dba)_3\cdot CHCl_3$[27], and $Pd(Cy_2PCH_2CH_2PCy_2)(\eta^2\text{-}CH_2{=}CH{-}CH{=}CH_2)$[51]. Complexes **1** and **14** display a slight distortion from the trigonal planar situation, as reflected by the twist around the metal-alken bond of 9.49(0.46)° for complex **1** and 9.84(0.13) and 5.99(0.13)° for complex **14**. Such a "tetrahedral" distortion is a known phenomenon in d^{10} metal-alkene complexes[1c]. The plane of best fit through the *p*-quinone residues and the coordination plane intersect at 78.57(0.49)° for **1** and at 94.29(0.23) and 99.91(0.21)° for **14**, indicating that the metal-alkene bond is approximately perpendicular to the plane of the *p*-quinone. The perpendicular coordination of the pbq moiety is depicted in Figure 4b by a side-on view of the coordination plane of **1**.

Figure 4a. Ortep drawing (30% probability level) of **1**

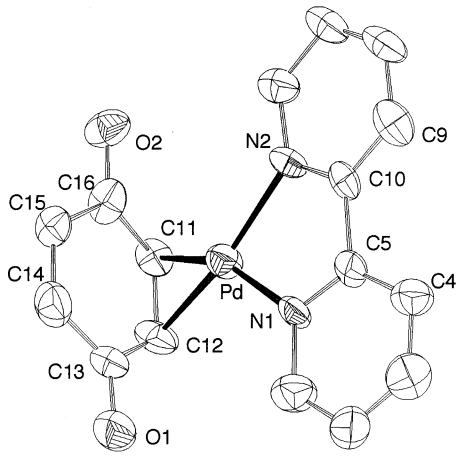


Figure 4b. Molecular plot of **1** viewed through the coordination plane

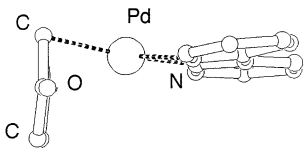


Table 1. Selected (bond) distances [Å] for the complexes **1**, **14**, and **16** (e.s.d.'s in parentheses)

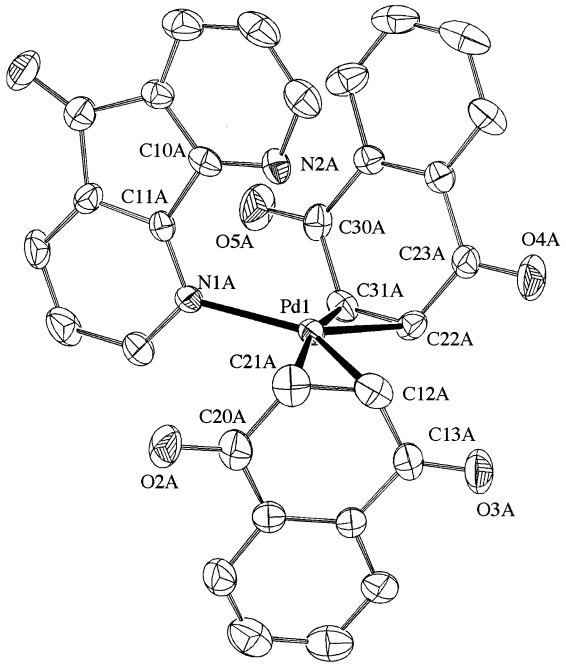
Pd(bpy)(pbq) (**1**)		Pd(dafo)(nq)$_2$ (**14**)		Pd_2(dafo)(pbq)$_2$ (**16**)	
				Pd(1)−Pd(2)	2.7747(4)
Pd−N(1)	2.121(12)	Pd(1)−N(1A)	2.1646(6)	Pd(1)−N(1)	2.166(4)
Pd−N(2)	2.101(11)	Pd(1)−N(2A)	3.070(5)	Pd(2)−N(2)	2.191(3)
Pd−C(11)	2.162(17)	Pd(1)−C(12A)	2.1764(7)	Pd(1)−C(12)	2.153(4)
Pd−C(12)	2.167(13)	Pd(1)−C(21A)	2.1558(7)	Pd(1)−C(13)	2.197(4)
O(1)−C(13)	1.27(2)	O(2A)−C(20A)	1.2137(9)	O(2)−C(14)	1.221(5)
O(2)−C(16)	1.255(19)	O(3A)−C(13A)	1.2188(10)	O(3)−C(20)	1.223(4)
N(1)−C(5)	1.340(17)	N(1A)−C(11A)	1.3286(10)	N(1)−C(5)	1.330(5)
N(2)−C(10)	1.299(19)	N(2A)−C(10A)	1.3188(10)	N(2)−C(10)	1.337(5)
C(5)−C(10)	1.53(2)	C(10A)−C(11A)	1.4709(11)	C(5)−C(10)	1.502(5)
C(11)−C(12)	1.43(2)	C(22A)−C(31A)	1.4293(13)	C(12)−C(13)	1.390(7)
C(14)−C(15)	1.38(2)	C(12A)−C(21A)	1.3937(11)	C(15)−C(16)	1.387(7)

Table 2. Selected bond angles [°] for the complexes **1**, **14**, and **16** (e.s.d.'s in parentheses)

Pd(bpy)(pbq) (**1**)		Pd(dafo)$(nq)_2$ (**14**)		Pd_2(dafo)$(pbq)_2$ (**16**)	
N(1)−Pd−N(2)	77.0(4)				
		N(1A)−Pd(1)−C(21A)	92.11(3)	N(1)−Pd(1)−C(12)	89.16(15)
		N(1A)−Pd(1)−C(31A)	95.46(3)	N(1)−Pd(1)−C(18)	97.13(13)
C(11)−Pd−C(12)	38.4(5)	C(12A)−Pd(1)−C(21A)	37.53(3)	C(15)−Pd(2)−C(16)	37.48(17)
		C(22A)−Pd(1)−C(31A)	38.54(3)	C(21)−Pd(2)−C(22)	37.33(14)
N(1)−Pd−C(12)	123.4(4)				
N(1)−C(5)−C(10)	115.6(12)	N(1A)−C(11A)−C(10A)	126.88(7)	N(1)−C(5)−C(10)	130.6(3)
N(2)−C(10)−C(5)	113.3(13)	N(2A)−C(10A)−C(11A)	126.36(7)	N(2)−C(10)−C(5)	130.3(3)
		C(12A)−Pd(1)−C(22A)	96.28(3)	C(13)−Pd(1)−C(19)	98.74(16)

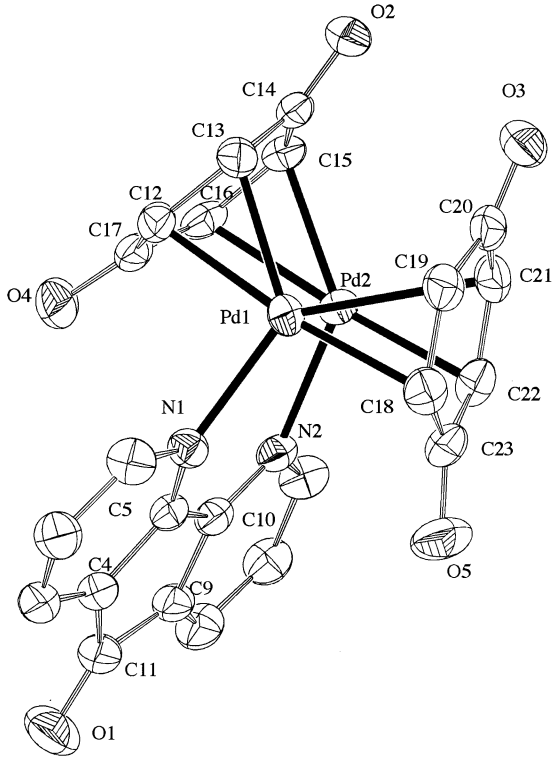
The alkenic and the carbonyl bonds in the *p*-quinone molecules in each of the three complexes are longer than in the free *p*-quinones[52], but the elongation of the coordinated C=C bond in **14** and **16** is less than in complex **1**, in which there are two nitrogen donor atoms instead of one. The carbonyl groups are bent away from the plane through the alkenic carbon atoms by 5.17(1.59) and 6.93(1.47)° for **1**, by 1.89(0.71), 0.43(0.42), 9.43(0.86), and 5.04 (0.83)° for **14**, and by 5.82(0.41), 0.74(0.41), 10.68(0.41), and 12.88(0.40)° for **16**.

Figure 5. Ortep drawing (30% probability level) of **14**



These angular distortions as well as elongations of the C=O double bonds in the *p*-quinone residue are comparable to those in $Pt(PPh_3)_2$(pbq)[30] and is also present in each of the previously reported structures with nickel−[53] and cobalt−*p*-quinone complexes[54]. In the case of **16**, the relatively large angular distortion of the carbonyl carbon atoms (vide supra) is mainly due to a steric interaction between the carbonyl groups of the two coordinated pbq moieties as is revealed by the view along the palladium palladium axis (Figure 6b). The distortion in the nitrogen ligands depends on the type of complex. Since dafo is monodentate coordinated in **14**, it shows no significant changes in bond angles and distances upon coordination compared with the free ligand[55]. However, in **16** the nitrogen ligand is distorted due to bridging coordination to two metal centers. The palladium atoms are not in the plane of the ligand; one palladium is positioned above and the other below the plane defined by N(1)C(5)C(10)N(2). The Pd(1)−Pd(2) vector intersects this plane by 7.72(0.35)°. This feature is nicely demonstrated in Figure 6c. The N(1)C(5)C(10) angle is 130.0° (free ligand 127.5°)[55] and the torsion angle N(1)C(5)C(10)N(2) is 11.3° (free ligand 0.0°). In complex **1**, due to the tetrahedral distortion, a torsion angle in the contiguous atoms N(1)C(5)C(10)N(2) of 7.43° is observed. The imine bonds in **1** and **16** are slightly elongated upon coordination in comparison with the free ligands.

Figure 6a. Ortep drawing (30% probability level) of **16**



The structure of the Pd(dafo)$(nq)_2$ complex (**14**) is unique, no similar complexes are known. An interesting feature of **14** is the non-bonding Pd(1A)−N(2A) distance of

Figure 6b. Plot of **16** viewed along the Pd(1)−Pd(2) axis

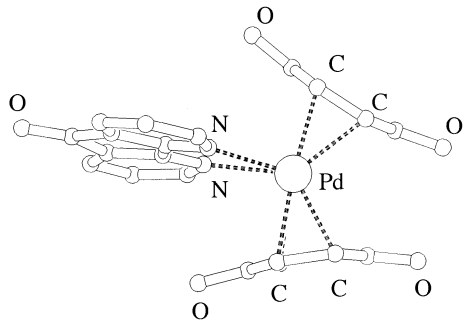
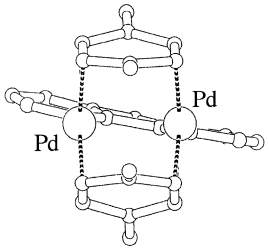


Figure 6c. Plot of **16** viewed through the Pd(1)−N(1)−N(2)−Pd(2) plane



3.070(5) Å, which is too long for any significant bonding interaction between these two atoms. This non-bonding Pd−N distance is longer than the similar Pt−N distance in $PtCl_2(Me_2\text{-phen})(PPh_3)_2$ [2.673(6) Å][56]. The N(2A) atom is approaching an apical position at palladium and does not intermolecularly coordinate towards another palladium. There is no tendency for **14** to form a dimeric palladium complex such as **16**, which is probably due to the steric bulk of the *p*-naphthoquinone compared to *p*-benzoquinone.

The solid-state structure of complex **16** is unprecedented but resembles that of $Pd_2(dba)_3$[50], however, in the latter the two palladium centers are bridged by three dienes instead of two as in **16**. The Pd(1)−Pd(2) distance in complex **16** [2.7747(4) Å] is significantly shorter than in $Pd_2(dba)_3\cdot CHCl_3$ [3.245(2) Å][27] and $Pd_2(dba)_3\cdot CH_2Cl_2$ [3.237(5) Å][50]. The short Pd-Pd distance in **16** is due to the smaller span and conformational restriction of the dafo ligand as compared to dba and is close to a Pd^I-Pd^I bond, which usually range from 2.53 to 2.75 Å[57][58][59][60][61][62].

IR Spectroscopy

The infrared spectra of the complexes all show a bathochromic shift of the stretching frequency ν(C=O) of the *p*-quinones as compared to the free *p*-quinone[63], the magnitude of which depends on the type of complex. In the M(N∩N-κ*N*)(η^2-nq)$_2$ complexes, ν(C=O) is only slightly shifted ($\Delta\nu$ = 5 cm^{-1}), wheras in the type $M_2(\mu^2$-N∩N)(μ^2,η^2:η^2-pbq)$_2$ this shift is approximately 30 cm^{-1} and in the type M(N∩N-κ^2*N*)(η^2-Q) it amounts to $\Delta\nu$ = 60 cm^{-1}. The latter shift is larger than for comparable structures reported, $\Delta\nu$(CO) = 44, 25, and 18 cm^{-1} in $PdL_2(\eta^2$-pbq) for L = *n*Bu_3P, Ph_3P, and PhO_3P, respectively[24] and 43 and 47 cm^{-1} in Pd(COD)(η^2-Q) for Q = pbq and nq, respectively[30]. In structures of the type $Pt(PPh_3)_2(\eta^2$-Q) in which the *p*-quinone represents a series of substituted derivatives[30], this shift is usually 30−60 cm^{-1}. These low-frequency shifts underscore the importance of the back donation from palladium to the *p*-quinone and is an indicative tool to determine the type of complex obtained, as ν(C=O) decreases with an increasing number of nitrogen donor atoms coordinated to the palladium relative to thenumber of *p*-quinone double bonds. The relative small shifts reported for complexes **1**−**24** indicate only a relatively minor perturbation of the C=O stretching mode, hence coordination is apparently only through the double bonds of the *p*-quinone moiety, as has been confirmed by the X-ray crystal structures determined for **1**, **14**, and **16**. For compounds in which the C=O function participates in the bonding, ν(C=O) decreases much more (150−200 cm^{-1})[22].

NMR Spectroscopy

The ^{1}H- and ^{13}C-NMR data for the complexes **1**−**24** show the expected high-frequency shift for the protons of the nitrogen ligands upon coordination. Compared to the free *p*-quinones[64], the alkenic protons of the coordinated *p*-quinone show a shift of 0.96−1.75 ppm to lower frequency, which is comparable to the shift for complexes Pd(COD)(η^2-pbq) ($\Delta\delta$ = 1.03 ppm) and Pd(COD)(η^2-nq) ($\Delta\delta$ = 1.94 ppm)[30]. However, these shifts are considerably smaller than the shifts reported for the complexes of the type M(L)$_2$(η^2-alkene) (M = Pd, Pt, alkene = dmfu, ma, fn) where they amount to 3−3.5 ppm[6]. The alkenic carbon atoms show for the complexes of the type Pd(N∩N-κ^2*N*)(η^2-Q) a shift of ca. 30 ppm to lower frequency in their ^{13}C-NMR spectra, and of ca. 60 ppm for the complexes of the type M(N∩N-κ*N*)(η^2-nq)$_2$ and $Pd_2(\mu^2$-N∩N)(μ^2,η^2:η^2-pbq)$_2$, in keeping with the considerable amount of back-donation from palladium to the *p*-quinone caused by the combination of an electron rich d^{10} metal center with a σ-donating α-diimine ligand. The low frequency shifts of the alkenic protons in the analogous platinum complexes are more pronounced than in the palladium complexes, which is due to the higher Lewis basicity of platinum.

The ^{1}H-NMR spectra of the complexes Pt(N∩N-κ^2*N*)(η^2-pbq), **18** and **19** show fluxional behaviour; at ambient temperature and 300.13 MHz the protons assigned to the pbq appear as a slightly broadened singlet (the platinum satellites are not observed) which broadens upon lowering the temperature. At 213 K two broadened singlets belonging to the pbq ligand are present. We ascribe this feature to a degenerate rearrangement in which the Pt(N∩N-κ^2*N*) moiety is alternatingly η^2-bonded to either of the two equivalent alkenic sites of *p*-benzoquinone. The free energy of activation ($\Delta G^{\neq}$) for this process was calculated[65] to be 50.3±1.0 kJmol^{-1} (241 K) for **18** and 52.1±1.0 kJmol^{-1} (238 K) for **19**. The slow exchange regime could be reached, in contrast to the observation for Pt(COD)(η^2-pbq) in which it could not be reached even at 183 K[25]. For **1**−**6**, the palladium analogues of **18** and **19**, slow exchange could not be reached at 180 K (300.13 MHz), only a slight broad-

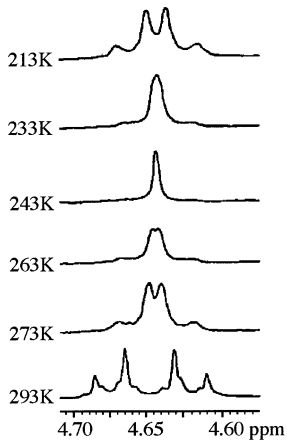
ening of the pbq-signal is observed. The ^{1}H-NMR data of the Pd(N∩N-κ^2*N*)(pbq) complexes (**1**−**6**) imply for the complexes in solution, either a rigid structure with the pbq η^4-bonded to the metal, or a low-energy degenerate rearrangement of a ground state η^2-bonded ligand. In view of the other results in solution and solid state, we prefer to assume the latter. For the platinum complexes it has been proven that in solution the latter assumption is true while clearly the rearrangement is in slow exchange at 213 K. Evidently, the rearrangement proceeds on the NMR time scale via an *intra*molecular process, since variation of the concentration had no effect on the free energy of activation of this rearrangement.

The complexes containing bpym, **6** and **11**, show dynamic behaviour resembling a previously described internal rotation of the two rings in bpym relative to each other in Pd(bpym)(η^3-allyl) compounds[66]. The exchange requires a cleavage of a Pd−N bond, i.e. a mechanism is involved in which two-coordinate intermediate complexes[67] exist in which the bidentate nitrogen ligand is coordinated in a monodentate way. The observed free energies of activation for this internal rotation are similar to those reported[66], $\Delta G^{\neq}$ = 53.7±1.0 kJmol^{-1} (243 K) for **6** and $\Delta G^{\neq}$ = 52.1±1.0 kJmol^{-1} (251 K) for **11**.

In complexes Pd(N∩N-κ*N*)(η^2-nq)$_2$ (**14**, **15**), both halves of the nitrogen ligand, which coordinates in a monodentate way, show identical chemical shifts in the ^{1}H- as well as in the ^{13}C-NMR spectra down to 160 K. We assign this behaviour to fast exchange between alternatingly coordinating N atoms of the ligand towards the palladium atom, representing a ligand flipping process analogous to that described by Natile[56]. These authors observed that, for Pt(2,9-dimethyl-1,10-phen)(PPh_3)Cl_2, in which the phenanthroline ligand coordinates in a monodentate way, the ligand flipping could be stopped at 150 K and splitting of the ligand signals is observed. The alternative, which is in agreement with the ^{1}H-NMR spectra, is the existence of the complexes **14** and **15** as tetrahedral 18e complexes in which the nitrogen ligand coordinates in a bidentate mode. However, in view of the solid state structure of **14** and the exchange experiments with *p*-quinones, which showed that complexes of type Pd(N∩Nκ^2*N*)(η^2-nq)$_2$ could be obtained for dafo and dafe ligands, but *not* in the cases utilizing bpy, phen etc., we reject this possibility. Adopting the view that the structure in solution is the same as the one in the solid state, i.e. a 16e complex with monodentate coordinating nitrogen ligand, the observations are easily explained on the basis of the different geometrical constraints of dafo and dafe (i.e. the larger bite angle) as compared to bpy and phen (see the introduction). In the case of **14**, and **15**, concomitantly with the ligand flipping another dynamic process takes place, as witnessed by a broadened singlet for the nq signals, indicating that the *p*-quinones are rotating. For this process, the slow exchange limit could not be reached (170 K at 300 MHz).

A peculiar dependence of the ^{1}H-NMR spectra of the complexes $Pt_2(\mu^2$-dafo)$(\mu^2,\eta^2{:}\eta^2$-pbq)$_2$ (**24**), $Pd_2(\mu^2$-dafo)$(\mu^2,\eta^2{:}\eta^2$-pbq)$_2$ (**16**) and $Pd_2(\mu^2$-dafe)$(\mu^2,\eta^2{:}\eta^2$-pbq)$_2$ (**17**) on the temperature has been observed. In the ^{1}H-NMR spectrum of the Pt compound **24**, the protons of pbq appear at 300.13 MHz as an A_2B_2 pattern with Δν(A−B) = 177 Hz, *J*(Pt,H) = 87.7 and 29.7 Hz. Cooling down the sample in $CDCl_3$ to 218 K showed a temperature dependence of the shifts for A and B as Δν(A−B) decreased by 30 Hz. The protons of pbq in the $Pd_2(\mu^2$-N∩N$)(\mu^2$-pbq$)_2$ complexes appear, in agreement with the solid state structure, at 293 K as an AA′BB′ pattern as is shown by the bottom spectrum in Figure 7. Simulation of the spectra (300.13 MHz) showed that for **16** Δν(A−B) = 9 Hz and the coupling constants are 8.3, 2.2, and 0.2 Hz. For **17** these values are Δν = 27 Hz and *J* = 8.2, 2.1, and 0.2 Hz. When cooling the sample to 253 K, the signal reverts into a singlet, upon further cooling to 213 K the pbq signal appears again as an AA′BB′ pattern albeit rather broadened (top spectrum, Figure 7; the latter broadening is probably due to the viscosity of the solvent at this temperature). We ascribe this process, on the basis of the observations made for the analogous platinum complex **24**, vide supra, to a temperature dependence of the chemical shift of the protons involved.

Figure 7. Variable-temperature ^{1}H-NMR of CH protons of pbq in **16**



Conclusion

A remarkable difference in coordination behaviour is observed between bidentate nitrogen ligands dafo and dafe and the other nitrogen ligands used in this study. In the case of dafo and dafe, exceptional Pd(N∩N-κ*N*)(η^2-nq)$_2$ and $Pd_2(\mu^2$-N∩N$)(\mu^2,\eta^2{:}\eta^2$-pbq$)_2$ complexes are formed. The monodenate or bridging coordination of the N∩N ligand in these instances is mainly a consequence of the annelation on the 3,3′-position of 2,2′-bipyridine by one carbon atom, by virtue of which the bite-angle of the ligands dafo and dafe is slightly but significantly larger compared to those of 2,2′-bipyridyl, phenanthroline, Ar-bian, and open-chain diazabutadienes. The stoichiometry in the Pd_x(N∩N)$(Q)_2$ complexes where N∩N = dafo or dafe depends on the nature of the *p*-quinone.

We thank the *Organization for the Advancement of Pure Research* (SON/NWO) and the *Stichting John van Geuns Fonds* for financial support for obtaining NMR instruments.

Experimental Section

General: All experiments were carried out using standard Schlenk techniques, under an atmosphere of dry nitrogen. The solvents were dried according to standard procedures and distilled before use. − ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 300 NMR spectrometer at 300.13 and 75.48 MHz, respectively. Chemical shift values are in ppm relative to TMS as external standard with high frequency shifts signed positive (protons are numbered according to Figure 2). Abbreviations used are s = singlet, d = doublet, t = triplet, pst = pseudo triplet, q = quartet, sep = septet, m = multiplet, br = broad; multiplicity, coupling constants (Hz) and number of protons in parenthesis. − IR spectra (KBr) were recorded on a Biorad FTS-7 IR spectrometer; abbreviations used: s = strong, m = medium, w = weak, br = broad, sh = shoulder. − Elemental analysis were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. − Mass spectra (FAB) were recorded by the Institute of Mass spectroscopy of the University of Amsterdam. − Dibenzylideneacetone (dba)[68], $Pd(dba)_2$[69], $Pt(dba)_2$[70], 4,5-diazafluoren-9-one (dafo)[19], 4,5-diazafluorene (dafe)[20], 5,6-dihydro-1,10-phenanthroline (dh-phen)[20], *N,N′*-dicyclohexyl-1,4-diaza-1,3-butadiene (chex-dab)[71][72] and bis[*N*-(*o,o′*-diisopropyl)phenylimino]-acenaphthene (*o,o′*-*i*Pr2-bian)[7] were synthesized according to published procedures. The *p*-quinones (Q) 1,4-benzoquinone (pbq) and 1,4-naphthoquinone (nq) and the *N*-ligands 2,2′-bipyridine (bpy), 2,2′-bipyrimidine (bpym), and 1,10-phenanthroline (phen) are commercially available and were used as received. Compounds **1**[39], **2**, **7** and **8** are known[27].

Synthesis of Palladium Complexes Pd(N∩N)(Q) (**1**−**3**, **7**, **8**, **12**, **13**): A typical procedure for the synthesis of [*(2,3-η)-1,4-benzoquinone](2,2′-bipyridine-k²N,N′)palladium(0)* (**1**), is given. $Pd(dba)_2$ (124.3 mg = 0.22 mmol), bpy (35.8 mg = 0.23 mmol), and pbq (26.8 mg = 0.25 mmol) were dissolved in toluene (60 ml) and stirred for thirty minutes at 20°C. The colour of the solution changed from dark purple to yellow and a dark compound precipitated. A solid was separated, which was dissolved in dichloromethane (50 ml) and this solution was filtered through Celite to remove metallic palladium. The solution was concentrated to ca. 5 ml and the product was precipitated with hexane (30 ml). The precipitate was filtered off and washed twice with toluene (30 ml), twice with ether (30 ml), and with hexane (30 ml) and dried under vacuum which gave a red brown solid (85%). The analogous complexes were synthesized in a similar way. The yields ranged from 84 to 93%. Dark red crystals of suitable for an X-ray crystal structure determination were obtained by slow diffusion of hexane in a solution of **1** in dichloromethane at 4°C.

(2,2′-Bipyridine-k²N,N′)[(2,3-η)-1,4-Benzoquinone]-palladium(0) (**1**): ^{1}H NMR ($CDCl_3$, 293 K): 8.55 (d, 4.7, H1), 8.09 [d, 7.9, H(X)], 8.01 (dd, 7.9, 7.9, H2), 7.53 (dd, 7.9, 4.7, H3), 5.71 [s, H(pbq)]. − ^{13}C NMR ($CDCl_3$, 213 K): 178.3 (s, *C*=O), 153.8 (s), 150.7 (d), 140.1 (d), 127.7 (s), 122.5 (d), 103.5 (d). − IR: 1602 (s, br). − Mass found *m/z* = 371 (calcd. = 370.7).

(1,10-Phenanthroline-k²N,N′)[(2,3-η)-1,4-benzoquinone]-palladium(0) (**2**): ^{1}H NMR ($CDCl_3$, 293 K): 8.90 (d, 4.7, H1), 8.47 (d, 8.2, H3), 7.83 (dd, 8.2, 4.7, H2), 7.95 [s, H(X)], 5.79 [s, H(pbq)]. − ^{13}C NMR ($CDCl_3$, 213 K): 179.0 (s, *C*=O), 150.7 (d), 145.8 (s), 138.8 (d), 129.8 (s), 127.8 (d) 126.4 (d), 103.3 (d). − IR: 1585 (s, br). − Mass found *m/z* = 397 (calcd. 396.4).

(5,6-Dihydro-1,10-phenanthroline-k²N,N′)[(2,3-η)-1,4-benzoquinone]palladium(0) (**3**): ^{1}H NMR ($CDCl_3$, 293 K): 8.32 (d, 5.0, H1), 7.72 (d, 7.7, H3), 7.40 (dd, 7.7, 5.0, H2), 5.79 [s, br, H(pbq)], 3.13 [s, H(X)]. − ^{13}C NMR ($CDCl_3$, 273 K): 189.6 (s, *C*=O), 151.4 (s), 148.8 (d), 138.6 (d), 135.3 (s), 127.1 (d), 102.4 (d), 26.7 (t). − IR: 1588 (s, br). − Mass found *m/z* = 397 (calcd. = 396.7).

(2,2′-Bipyridine-k²N,N′)[(2,3-η)-1,4-naphthoquinone]-palladium(0) (**7**): ^{1}H NMR ($CDCl_3$, 293 K): 8.58 [d, 5.1, H1(NN)], 8.06 [m, H3(NN) + H2(nq)], 7.92 [m, H2(NN)], 7.46 [m, H(X) + HH3(nq)], 4.97 [s, br, H1(nq)]. − ^{13}C NMR ($CDCl_3$, 293 K): (*C*=O not observed), 153.9 (s), 151.2 (d), 139.2 (d), 133.2 (s), 129.6 (d), 127.2 (d), 125.7 (d), 121.8 (d), 105.0 (d). − IR: 1617 (s, br). − Mass found *m/z* = 421 (calcd. 420.7).

(1,10-Phenanthroline-k²N,N′)[(2,3-η)-1,4-naphthoquinone]-palladium(0) (**8**): ^{1}H NMR ($CDCl_3$, 293 K): 8.94 [d, 4.7, H1(NN)], 8.37 [d, 8.2, H2(nq)], 8.07 [m, H3(nq)], 7.82 [s, H(X)], 7.79 [dd, 8.2, 4.7, H2(NN)], 7.42 [m, H3(NN)], 5.01 [s, H1(nq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1617 (s, br). − Mass found *m/z* = 447 (calcd. 446.9).

(4,5-Diazafluoren-9-one-k²N,N′)[(2,3-η)-1,4-naphthoquinone]-palladium(0) (**12**): ^{1}H NMR ($CDCl_3$, 293 K): 8.02 [d, 7.6, H1(NN)], 7.93 [m, H3(NN) + H2(nq)], 7.58 [m, H3(nq)], 7.38 [dd, 7.6, 5.4, H2(NN)], 5.66 [s, br, H1(nq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1629 (s), 1727 (s, dafo). − Mass found *m/z* = 447 (calcd. 446.7).

(4,5-Diazafluorene-k²N,N′)[(2,3-η)-1,4-naphthoquinone]-palladium(0) (**13**): ^{1}H NMR ($CDCl_3$, 293 K): 8.33 [m, br, H1(NN)], 7.94 [m, H3(NN) + H2(nq)], 7.48 [m, H3(nq)], 7.40 [m, H2(NN)], 5.12 [s, H1(nq)], 4.03 [s, H(X)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1626 (s). − Mass found *m/z* = 433 (calcd. 432.8).

Synthesis of Palladium Complexes Pd(N∩N)(Q) (**4**−**6** and **9**−**11**): A typical procedure for the synthesis of *[(2,3-η)-1,4-benzoquinone](o,o′-iPr₂-bian-k²N,N′)palladium(0)* (**5**) is given. $Pd(dba)_2$ (124.3 mg = 0.22 mmol), *o,o′*-*i*Pr_2-bian (115.1 mg = 0.23 mmol), and pbq (26.8 mg = 0.25 mmol) were dissolved in acetone (50 ml) and stirred for thirty minutes at 20°C. It was difficult to see a clear colour change although the colour of the solution slightly changed from dark purple to dark red. The solution was filtered to remove the metallic palladium and the solution was concentrated to a fraction of its original amount. The product was precipitated with hexane (30 ml) and washed twice with ether (30 ml) and with hexane (30 ml) and dried under vacuum which gave a red brown solid (87%). The other complexes were synthesized in a similar way. The yields ranged from 87 to 95%.

(N,N′-Dichexyl-1,4-diaza-1,3-butadiene-k²N,N′)[(2,3-η)-1,4-benzoquinone]palladium(0) (**4**): ^{1}H NMR ($CDCl_3$, 293 K): 8.06 (s, NN), 5.47 [s, H(pbq)], 3.45 [m, NC*H*(*c*hex)], 1.90−1.28 [m, (*c*hex)]. − ^{13}C NMR ($CDCl_3$, 293 K): 186.6 (s, *C*=O), 156.6 (d), 98.9 (d), 71.0 (d), 32.8 (t), 24.3 (t), 24.2 (t). − IR: 1615, 1634. − Mass found *m/z* = 435 (calcd. 435.4).

Bis(o,o′-diisopropylphenylimino)-acenaphtene-k²N,N′)[(2,3-η)-1,4-benzoquinone]palladium(0) (**5**): ^{1}H NMR ($CDCl_3$, 293 K): 8.03 (d, 8.3, H3), 7.16 (pst, H2), 7.36 [m, H(Ph)], 6.73 (d, 11.7, H1), 5.28 [s, H(pbq)], 3.29 [sept, 6.8, (C*H*, *i*Pr)], 1.43 [d, 6.8, (CH_3, *i*Pr)], 0.96 [d, 6.9, (CH_3, *i*Pr)]. − ^{13}C NMR ($CDCl_3$, 293 K): 185.2 (s, *C*=O), 167.1 (s), 143.4 (s), 142.9 (s), 137.2 (s), 131.1 (s), 130.6 (d), 128.6 (d), 127.0 (s), 126.9 (s), 124.14 (d), 123.7 (d), 99.0 (d), 28.7 (d), 23.3 (q), 22.9 (q). − IR: 1623. − Mass found *m/z* = 715 (calcd. = 715.8).

(2,2′-Bipyrimidine-k²N,N′)[(2,3-η)-1,4-benzoquinone]-palladium(0) (**6**): ^{1}H NMR ($CDCl_3$, 293 K): 8.95 (s, br, H1), 7.66 (pst, H2), 5.82 [s, br, H(pbq)]. − ^{13}C NMR ($CDCl_3$, 293 K): 189.2 (s, *C*=O), 159.8 (s), 158.1 (d), 121.6(d), 10.2 (d). − IR: 1645 (s).

(N,N'-Dichexyl-1,4-diaza-1,3-butadiene-k²N,N')[(2,3-η)-1,4-naphthoquinone]palladium(0) (**9**): ^{1}H NMR ($CDCl_3$, 293 K): 7.98 [m, H2(nq)], 7.96 (s, NN), 7.48 [m, H3(nq)], 4.59 [s, H1(nq)], 3.40 [m, NC*H*(*c*hex)], 1.88-1.28 [m, (*c*hex)]. − ^{13}C NMR ($CDCl_3$, 293 K): 184.7 (s, *C*=O), 156.3 (d), 136.1 (s), 131.0 (d), 124.9 (d), 71.1 (d), 32.9 (t), 32.4 (t), 24.2 (t), =*C*H (nq) not observed. − IR: 1622 (s), 1633 (sh). − Mass found *m/z* = 485.15 (calcd. 484.88). − $C_{24}H_{30}N_2O_2Pd$: found (calcd.): C, 59.28 (59.44), H, 6.256 (6.24), N, 5.65 (5.77).

(o,o'-iPr₂-bian-k²N,N')[(2,3-η)-1,4-Naphthoquinone]palladium(0) (**10**): ^{1}H NMR ($CDCl_3$, 293 K): 7.99 [d, 8.3, H3(NN)], 7.83 [dd, 7.0, 3.6, H2(NN)], 7.51−7.28 [m, 10 H (NN + nq)], 6.64 [d, 7.23, H1(NN)], 4.46 [s, H1(nq)], 3.50 [sept, 6.7, (C*H*, *i*Pr)], 2.78 [sept, 6.7, (C*H*, *i*Pr)], 1.54 [d, 6.4, (C*H*$_3$, *i*Pr)], 1.02 [d, 6.4, (C*H*$_3$, *i*Pr)], 1.01 [d, 6.7, (C*H*$_3$, *i*Pr)], 0.76 [d, 6.7, (C*H*$_3$, *i*Pr)]. − ^{13}C NMR ($CDCl_3$, 293 K): 183.3 (s, *C*=O), 166.9 (s), 143.2 (s), 139.8 (s), 137.5 (s), 137.1 (s), 135.7 (s), 131.1 (s), 130.4 (d), 128.5 (d), 126.9 (d), 126.9 (s), 125.2 (d), 124.1 (d), 123.8 (d), 123.5 (d), 58.7 (d), 28.7 (d), 28.6 (d), 23.6 (q), 23.1 (q), 22.8 (q), 22.7 (q). − IR: 1639 (s). − Mass found *m/z* = 765.27 (calcd. 765.23). − $C_{46}H_{46}N_2O_2Pd$: found (calcd.): C, 71.11 (71.29), H, 6.16 (6.26), N, 3.66 (3.78).

(2,2'-Bipyrimidine-k²N,N')[(2,3-η)-1,4-naphthoquinone]palladium(0) (**11**): ^{1}H NMR ($CDCl_3$, 293 K): 8.97 [s, br, H1(NN)], 8.05 [m, H2(nq)], 7.63 [pst, H2(NN)], 7.45 [m, H3(nq)], 4.89 [s, H1(nq)]. − ^{13}C NMR ($CDCl_3$, 293 K): 180.5 (s, *C*=O), 158.9 (s), 157.9 (d), 136.1 (s), 131.3 (d), 125.1 (d), 123.7 (d), =*C*H (nq) not observed. − IR: 1620 (s, br). − Mass found *m/z* = 423.01 (calcd. 422.68).

Synthesis of Platinum Complexes Pt(N∩N)(Q) (**18−21**): The platinum complexes **18−21** were synthesized in a similar way as **1**, but distinctly longer reaction times were needed (14 h at 20°C) and the yields ranged from 73 to 85%.

[(2,3-η)-1,4-Benzoquinone](2,2'-bipyridine-k²N,N')platinum(0) (**18**): ^{1}H NMR ($CDCl_3$, 293 K): 9.00 (d, 5.1, J_{Pt-H}: 33.4, H1), 8.10 (m, H2), 8.09 (m, H3), 7.55 [d, 5.1, H(X)], 5.49 [s, br, H(pbq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1617 (s, br). − Mass found *m/z* = 460 (calcd. 459.4).

(1,10-Phenanthroline-k²N,N')[(2,3-η)-1,4-benzoquinone]platinum(0) (**19**): ^{1}H NMR ($CDCl_3$, 293 K): 9.32 (d, 5.0, J_{Pt-H}: 31.1, H1), 8.59 (d, 8.2, H3), 7.79 [s, H(X)], 7.87 (dd, 8.2, 5.0, H2), 5.56 [s, br, H(pbq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1617 (s, br). − Mass found *m/z* = 484 (calcd. 483.4).

(2,2'-Bipyridine-k²N,N')[(2,3-η)-1,4-naphthoquinone]platinum(0) (**20**): ^{1}H NMR ($CDCl_3$, 293 K): 9.01 [d, 5.0, J_{Pt-H}: 31.5, H1(NN)], 8.10 [m, H2(nq)], 8.04 [d, 8.0, H(X)], 7.79 [d, 8.0, H2(NN)], 7.52 [dd, 8.0, 5.0, H3(NN)], 7.48 [m, H3(nq)], 4.60 [s, J_{Pt-H}: 75.9, H1(nq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1625 (s). − Mass found *m/z* = 510 (calcd. 509.4).

(1,10-Phenanthroline-k²N,N')[(2,3-η)-1,4-naphthoquinone]platinum(0) (**21**): ^{1}H NMR ($CDCl_3$, 293 K): 9.33 [d, 4.9, J_{Pt-H}: 31.1, H1(NN)], 8.50 [d, 8.2, H3(NN)], 8.11 [m, H2(nq)], 7.87 [s, H(X)], 7.84 [dd, 8.2, 4.9, H2(NN)], 7.44 [m, H3(nq)], 4.74 [s, J_{Pt-H}: 76.1, H1(nq)]. − ^{13}C NMR not recorded due to low solubility and instability. − IR: 1625 (s). − Mass found *m/z* = 534.078 (calcd. 533.4).

Synthesis of Palladium Complexes Pd(N∩N)(Q)₂ (**14**, **15**): These compounds can be synthesized in two ways, either in one or in two steps, and both methods will be described here.

Method A: (4,5-Diazafluoren-9-one-κN)bis[(2,3-η²)-1,4-naphthoquinone]palladium(0) (**14**): To a brown/red solution of Pd(dafo)(nq) **12** (44.8 mg = 0.1 mmol) in dichloromethane (50 ml) was added naphtoquinone (nq) (15.9 mg = 0.1 mmol), and the solution turned green/yellow after several minutes at 20°C. The same work-up procedure as for the Pd(N∩N)(Q) complexes was followed and this gave a green/yellow solid (83%).

Method B: Pd(dafo)(nq)₂ (**14**) *and Pd(dafe)(nq)₂* (**15**): $Pd(dba)_2$ (140.5 mg = 0.24 mmol), dafo (0.25 mmol), and nq (79.1 mg = 0.50 mmol) were dissolved in 40 ml of toluene and stirred for two hours at 20°C. The colour of the solution changed from dark purple to yellow and a dark compound precipitated. The same work-up procedure as for the Pd(N∩N)(Q) complexes was followed and this gave a green/yellow solid (yield: 93% for **14** and 87% for **15**). Orange crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane in a solution of **14** in dichloromethane/methanol (1:1, v/v) at 4°C.

(4,5-Diazafluoren-9-one-κN)bis[(2,3-η²)-1,4-naphthoquinone]palladium(0) (**14**): ^{1}H NMR ($CDCl_3$, 293 K): 8.01 [d, 7.4, H1(NN)], 7.78 [m, H3(NN) + H2(nq)], 7.49 [m, H3(nq)], 7.28 [dd, 7.4, 5.4, H2(NN)], 5.19 [s, H1(nq)]. − ^{13}C NMR ($CDCl_3$, 223 K): 188.5 (s, *C*=O), 185.4 (s, *C*=O), 161.4 (s), 154.7 (d), 133.8 (d), 133.7 (s), 133.5 (d), 130.6 (s), 127.1 (d), 126.5 (d), 80.9 (d). − IR: 1653 (s, br), 1730 (s, dafo). − Mass found *m/z* = 628 ([M+Na]$^{+\cdot}$) (calcd. 627.9). − $C_{31}H_{18}N_2O_5Pd$: found (calcd.): C, 58.74 (58.15), H, 2.76 (2.83), N, 4.28 (4.37).

(4,5-Diazafluorene-κN)bis[(2,3-η²)-1,4-naphthoquinone]palladium(0) (**15**): ^{1}H NMR ($CDCl_3$, 293 K): 8.02 [d, 7.7, H1(NN)], 7.89 [m, H3(NN) + H2(nq)], 7.52 [m, H3(nq)], 7.32 [dd, 7.7, 5.1, H2(NN)], 5.47 [s, H1(nq)], 3.98 [s, H(X)]. − ^{13}C NMR ($CDCl_3$, 223 K): 185.4 (s, *C*=O), 157.1 (s), 149.3 (d), 134.7 (d), 133.8 (s), 133.5 (d), 139.3 (s), 126.3 (d), 125.0 (d), 33.3 (t), =*C*H (nq) not observed. − IR: 1657 (s, br). − Mass found *m/z* = 433 (calcd. 591.0), the found mass corresponds to [Pd(dafe)(nq)]$^+$.

Synthesis of Platinum Complexes Pt(N∩N)(Q)₂ (**22**, **23**): The analogous platinum complexes **22**, **23** were synthesized in a similar way according to method B as described above but again longer reaction times were needed (14 hrs at 20°C). The yields were 75 and 78% respectively.

(4,5-Diazafluoren-9-one-κN)bis[(2,3-η²)-1,4-naphthoquinone]platinum(0) (**22**): ^{1}H NMR ($CDCl_3$, 293 K): 8.05 [d, 7.6, H1(NN)], 7.78 [m, H3(NN) + H2(nq)], 7.47 [m, H3(nq)], 7.30 [dd, 7.6, 5.4, H2(NN)], 4.77 [s, br, H1(nq)]. − ^{13}C NMR ($CDCl_3$, 223 K): 188.7 (s, *C*=O), 187.9 (s, *C*=O), 134.3 (d), 134.0 (s), 133.8 (d), 133.4 (d), 130.6 (s), 125.9 (d), 67.9 (d), *C*=N (s) and *C*=N (d) not observed. − IR: 1654 (s), 1731 (s, dafo). − Mass found *m/z* = 716 ([M+Na]$^+$) (calcd. 716.6). − $C_{31}H_{18}N_2O_5Pt$: found (calcd.): C, 49.65 (49.09), H, 2.79 (2.39), N, 3.91 (3.69).

(4,5-Diazafluorene-κN)bis[(2,3-η²)-1,4-naphthoquinone]platinum(0) (**23**): ^{1}H NMR ($CDCl_3$, 293 K): 7.92 [d, 7.9, H1(NN)], 7.73 [m, H3(NN) + H2(nq)], 7.43 [m, H3(nq)], 7.23 [m, H2(NN)], 4.75 [s, br, H1(nq)], 3.98 [s, H(X)]. − ^{13}C NMR ($CDCl_3$, 223 K): 189.1 (s, *C*=O), 134.5 (s), 134.1 (s), 133.6 (d), 133.3 (d), 127.2 (d), 125.8 (d), 67.8 (d), 33.3 (t), *C*=N (s) and *C*=N (d) not observed. − IR: 1666 (s, br). − Mass found *m/z* = 702 ([M+Na]$^+$) (calcd. 702.6).

Synthesis of Palladium Complexes Pd₂(N∩N)(Q)₂ (**16**, **17**): A typical procedure for the synthesis of *bis{[μ-(2,3-η²:5,6-η²)]-1,4-benzoquinone}-μ-(4,5-diazafluoren-9-one-k²N,N')bis-[palladium(0)]* (**16**) is given. $Pd(dba)_2$ (140.5 mg = 0.24 mmol), dafo (0.12 mmol) and pbq (25.9 mg = 0.24 mmol) were dissolved

in toluene (50 ml) and stirred for fifteen minutes at 20°C. The colour of the solvent changed from dark purple to yellow and a dark green compound precipitated. This solid was washed with toluene (2 × 20 ml) and with diethylether (2 × 20 ml). In order to remove the metallic palladium the compound was dissolved in dichloromethane and filtered through Celite. The solution was evaporated to a fraction of its original amount and the product was precipitated with hexane. The remaining yellow green solid was dried in vacuum (yield: 90% for **16** and 88% for **17**). Dark green crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane in a solution of **16** in dichloromethane/methanol (1:1, v/v) at 4°C.

Bis{[μ-(2,3-η²:5,6-η²)]-1,4-benzoquinone}-μ-(4,5-diazafluoren-9-one-k²N,N′)bis[palladium(0)] (**16**): ^{1}H NMR ($CDCl_3$, 293 K): 8.79 (d, 5.5, H1), 8.31 (d, 7.6, H3), 7.48 (dd, 7.6, 5.5, H2), 4.45 [ddd, 8.3, 2.2, 0.2, H(pbq)], 4.48 [ddd, 4.0, 1.0, 0.1, H(pbq)]. − ^{13}C NMR not recorded due to low solubility. − IR: 1629 (s, br), 1726 (s, dafo). − Mass found *m/z* = 634 ([M+Na]$^+$) (calcd. = 634.2). − $C_{23}H_{14}N_2O_5Pd_2$: found (calcd.): C, 44.57 (45.20), H, 2.65 (2.31), N, 4.38 (4.58).

Bis{[μ-(2,3-η²:5,6-η²)]-1,4-benzoquinone}-μ-(4,5-diazafluorene-k²N,N′)bis[palladium(0)] (**17**): ^{1}H NMR ($CDCl_3$, 293 K): 8.75 (d, 4.5, H1), 8.16 (d, 7.6, H3), 7.40 (dd, 7.6, 4.5, H2), 4.65 [ddd, 8.2, 2.1, 0.2, H(pbq)], 4.56 [ddd, 8.2, 2.1, 0.2, H(pbq)], 4.07 (s). − ^{13}C NMR (CD_2Cl_2, 293 K): 189.1 (s, *C*=O), 154.2 (d), 146.7 (s), 138.0 (d), 125.6 (d), 83.0 (d), 79.6 (d), 34.3 (t), *C*=CH (s, dafe) not observed. − IR: 1634 (s, br). − Mass found *m/z* = 597 (calcd. 597.2).

Synthesis of Platinum Complexe $Pt_2(N\cap N)(Q)_2$ (**24**): The analogous platinum complex **24** was synthesized similarly, but a reaction time of 14 hrs was required; the yield was 71%.

Bis{[μ-(2,3-η²:5,6-η²)]-1,4-benzoquinone}-μ-(4,5-diazafluoren-9-one-k²N,N′)bis[platinum(0)] (**24**): ^{1}H NMR ($CDCl_3$, 293 K): 8.83 (d, 5.5, J_{Pt-H}: 29.7, H1), 8.39 (d, 7.6, H3), 7.49 (dd, 7.6, 5.7, H2), 4.45 [d, 7.5, J_{Pt-H}: 87.7, H(pbq)], 3.86 [d, 7.5, J_{Pt-H}: 44.6, H(pbq)]. − ^{13}C NMR not recorded due to low solubility. − IR: 1640 (s, br), 1733 (s, dafo).

p-Quinone Substitution Reactions: *p*-Quinone substitution reactions were carried out for several combinations of complexes and *p*-quinones in varying stoichiometries. A typical experiment has been described below and the other substitution reactions proceeded in a similar way. *p*-Benzoquinone (11.2 mg = 0.1 mmol) was added to a solution of **7** (37.1 mg = 0.1 mmol) in dichloromethane (30 ml), which solution was then stirred for one hour at 20°C. After evaporation of the solvent the remaining solid was washed with diethylether (3 × 10 ml) and dried in vacuum. The residue as well as the organic products were analyzed with ^{1}H NMR spectroscopy.

X-ray Crystal Structure Determination: The crystal, collection, and refinement data of complexes **1**, **14**, and **16** have been compiled

Table 3. Crystallographic data for Pd(bpy)(pbq) **1**, Pd(dafo)(nq)$_2$ **14**, and Pd_2(dafo)(pbq)$_2$ **16**

Complex	**1**	**14**	**16**
Crystal data			
Formula	$C_{16}H_{12}N_2O_2Pd \cdot 2\ H_2O$	$C_{31}H_{14}N_2O_5Pd$	$C_{23}H_{14}N_2O_5Pd_2 \cdot CH_3OH$
Mol. weight	406.7	600.9	643.2
Cryst. system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*Pbn*2$_1$	*P*2$_1$/*c*
a [Å]	18.980(1)	10.909(4)	11.791(4)
b [Å]	7.627(7)	14.434(8)	12.470(3)
c [Å]	22.948(1)	30.391(2)	14.275(4)
α [°]	90	90	90
β [°]	108.572(4)	90	91.57(4)
γ [°]	90	90	90
V [Å^3]	3148.93(4)	4785.3(18)	2098.12(1)
Z	8	8	4
D_{calc} [g cm^{-3}]	1.72	1.682	2.03
μ [cm^{-1}]	99.3	67.9	17.4
F(000)	1632	2400	1264
crystal size [mm^3]	0.03 × 0.40 × 0.70	0.50 × 0.40 × 0.40	0.30 × 0.50 × 0.70
Collection			
T [K]	293	293	293
θ_{min}, θ_{max} [°]	4.1, 64.9	2.9, 69.9	1.7, 29.9
Radiation [Å]	1.5418 (Cu-*Kα*)	1.54180 (Cu-*Kα*)	0.71069 (Mo-*Kα*)
Scan type	ω/2θ	ω/2θ	ω/2θ
Acq. time [h]	60	57	80
Linear decay [%]	0	6	0
Ref. reflections	O(−,1) O(−,1) 1, 0 0 6	1 O(−,2) 4, 2 0 0	O(−,2) 2 3, 2 2 1
Data set (*h, k, l*)	21:20; −8:0; 0:26	0:13; −17:0; 0:36	−16:16; 0:17; 0:20
Total unique data	2576	4608	6067
Total obs. data	2216 [$I > 2.5\sigma(I)$]	4359 [$F_o > 4\sigma(F_o)$]	4950 [$I > 2.5\sigma(I)$]
DIFABS corr. range	0.55−1.91	0.668−1.509	0.91−1.34
Refinement			
Refined params	255	705	379
Final *R* [a]	0.102	0.0422	0.030
Final R_w [b]	0.163	−	0.049
Final *wR2* [c]	−	0.112	−
w^{-1} [d]	$6.6+F_o+0.0071F_o^2$	$\sigma F^2+0.831P^2+3.20P$	$9.5+F_o+0.0063F_o^2$
$(\Delta/\sigma)_{max}$	0.16	0.01	0.66
ρ_{min}, ρ_{max} (e Å^{-3})	−2.5, 6.1	−1.13, 2.99	−0.9, 0.6

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, − [b] $R_w = \{\Sigma[w(||F_o| - |F_c||)^2]/\Sigma[w(F_o^2)]\}^{0.5}$. − [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{0.5}$. − [d] $P = [\mathrm{Max}(F^2_{obs},0) + 2F^2_{calc}]/3$.

in Table 3. Data collection for these crystals was performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-*Kα* radiation for **1** and **14** and Mo-*Kα* radiation for **16** and ω-2θ scan. Two reference reflections were measured hourly and showed no decrease during the course of the data collection for the complexes **1** and **16** and 6% decrease for complex **14**, which was corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 80<2θ<84° for **1**, 80.1<2θ<84.9° for **14**, and 40<2θ<42° for complex **16**. Corrections for Lorentz and polarization effects were applied. The structure of the complexes **1** and **16** was solved by Direct Methods while the structure of **14** was solved by the PATTY option of the DIRDIF91 program system[73]. After isotropic refinements on **1** and **16**, peaks were found in a ΔF synthesis which were interpreted as water and methanol respectively which were used as solvents during crystallization. The hydrogen atoms were calculated. Full-matrix least-squares refinement on *F*, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to the R -values mentioned in Table 3. An empirical absorption correction, DIFABS[74] was applied. Scattering factors were taken from the literature[75][76][77]. Since the space group of complex **14** is polar, it was necessary to use the Flack absolute structure parameter[78], which refined to $x = 0.032(11)$. In case of the crystals of complex **14**, the matching of the two independent molecules for all non-hydrogen atoms resulted in a rms-value of 0.13 Å and a non-crystallographic center of symmetry is present (located at $x = 0.50$, $y = 0.37$, $z = 0.38$). The anomalous scattering of Pd was taken into account. For **1** and **16** calculations were performed with XTAL[79] and for **14** with SHELXL[80]. Thermal ellipsoid and molecular plots were made using the PLUTON and PLATON programs[81]. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited ar the Cambridge Crystallographic Data Centre, see instructions to authors. Any request to the CCDC for this material should quote the full literature citation and the reference number 100791.

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