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REACTIVITY OF CYCLOPALLADATED COMPOUNDS

VIII *. SYNTHESIS OF CYCLOMETALLATED COMPOUNDS WITH AN OXYGEN AS THE DONOR ATOM. CRYSTAL AND MOLECULAR STRUCTURE OF (8-METHYLQUINOLINE-*C,N*)-(1-METHOXYNAPHTHALENE-8-*C,O*)PALLADIUM(II)

J. DEHAND, A. MAURO, H. OSSOR, M. PFEFFER **,

Laboratoire de Chimie de Coordination ERA 670 du CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex (France)

R.H. DE A. SANTOS and J.R. LECHAT

Instituto de Quimica e Fisica de Sao Paulo, Universidade de Sao Paulo (Brazil)

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Summary

Treatment of 1-methoxynaphthalene (MXNH) with n-butyllithium in a diethyl ether/n-hexane solution gives 1-methoxynaphthalene-8-lithium (MXNLi) in 30% yield as an insoluble material. This compound reacts with $PdCl_2(SEt_2)_2$ to give bis(1-methoxynaphthalene-8-*C,O*)palladium(II) (I) and with $PtCl_2(SEt_2)_2$ to give *cis*- and *trans*-(1-methoxynaphthalene-8-*C,O*)(1-methoxynaphthalene-8-*C*)(diethylsulfide)platinum(II) (II), which are non-rigid molecules in solution. With the cyclopalladated dimers $[\{\overline{\text{Pd}(\text{C}-\text{N}})\text{Cl}\}_2]$, MXNLi gives the palladobicyclic compounds: $(\text{N}\cap\text{C})\text{Pd}(\text{C}\cap\text{O})$ (III). An X-ray diffraction study of compound IIIa where $\text{N}\cap\text{C}$ = 8-methylquinoline-*C,N* reveals the planarity of the molecule, shows that it has a *cis* configuration with respect to the Pd–C bonds, and confirms that the oxygen atom of MXN is bonded to palladium: Pd–O 2.236(4) Å. The geometry of IIIa is maintained in solution, whereas the corresponding compounds IIIb and IIIc in which $\text{N}\cap\text{C}$ is benzo[*h*]quinoline-9-*C,N* and *N,N*-dimethyl-1-naphthylamine-8-*C,N*, respectively, appear to be mixtures of *cis* and *trans* isomers in solution. With PMe_2Ph I and II give *trans*-$Pd(MXN)_2(PMe_2Ph)_2$ and *cis*-$Pt(MNX)_2(PMe_2Ph)_2$, respectively, in which the methoxynaphthalene is bound to the metals via the 8-carbon of the naphthalene ring. Only one phosphine ligand adds to compounds IIIb and IIIc with displacement of the O→Pd bond. One carbon monoxide ligand can be added to the

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* For Part VII see ref. 3a.

** To whom correspondence should be addressed.

platinum compound II to give $Pt(MXN)_2(SEt_2)CO$ which in solution exists as two isomers in equilibrium.

Cyclometallation involving ligands containing a donor atom of the Main Group V or VI by a transition metal has been extensively studied during the past 15 years [1], but to our knowledge very few examples of such reactions involving a ligand in which the donor atom is oxygen have been reported. Furthermore only complexes of transition metals such as manganese or rhenium have been found to undergo such reactions [2].

During the course of our study of the reactivity of cyclopalladated compounds [3] we became interested in the possibility of synthesis of metallocyclic molecules of palladium or platinum in which the donor atom is an oxygen, in order to compare their reactivity to the very well-known compounds in which the donor atom is a nitrogen atom. We postulated that these compounds should show enhanced reactivity since the O→M bond is usually much weaker than the N→M bond when M is a soft metal such as palladium or platinum [4]. In this paper we report the achievement of the first of these goals, viz. the synthesis of such compounds by reaction of lithiated 1-methoxynaphthalene with complexes of platinum and palladium. We also describe some characteristic reactions which illustrate the greater lability of the O→M bond than of the corresponding N→M bond.

Results and discussion

The lithiation reaction of 1-methoxynaphthalene (MXNH *) by n-butyllithium has been the subject of several reports in the literature [5]. The metallation can occur at either the 2- or the 8-position of the ring. Grayhill and Shirley showed that the metallation is very dependent on the nature of the n-BuLi used for the reaction [5c], and described a procedure by which a solid was obtained from the metallation, but they did not characterise it. In our hands the lithiation of 1-methoxynaphthalene with commercial n-butyllithium (1.6 *M* in n-hexane) in Et_2O produced ca. 30% of a light green solid. We have shown it to be pure 1-methoxynaphthalene-8-lithium; the ^1H NMR in $CDCl_3$ of the deuterated ligand obtained by reaction with D_2O shows the absence of the signal at ca. δ 8.3 ppm characteristic of the 8 proton [5c], whereas the ^2H NMR spectrum in $CDCl_3$ shows a single resonance at that chemical shift.

Synthesis of the oxygen containing metallocycles

We found that 1-methoxynaphthalene-8-lithium ("MXNLi") is a good starting material for production of metallocyclic species from platinum or palladium compounds. Thus the reaction of an excess of "MXNLi" with $PdCl_2(SEt_2)_2$ (3/1 ratio) in a THF solution affords a white crystalline compound I. The analysis suggests the formula: $Pd(MXN)_2$. The IR spectrum shows only absorptions of the 1-methoxynaphthalene group. The ^1H NMR spectrum in $CDCl_3$ shows a complex signal for the aromatic protons between δ 7.8 and 6.9 ppm together with a single resonance for the protons of the methoxy groups at δ 4.44 ppm (Table 1). This

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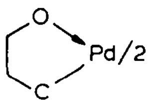
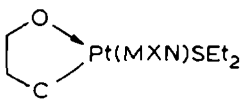
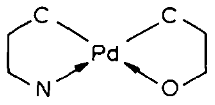
* Throughout this paper MXN represents the 1-methoxynaphthalene group substituted at position 8.



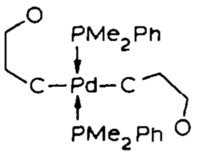
(I)



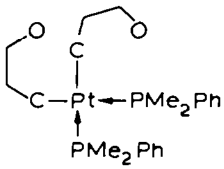
(IIa, *cis* ;
IIb, *trans*)



(IIIa, N⌒C = 8-mq ;
IIIb, N⌒C = B(h)q ;
IIIc, N⌒C = dmna)



(IV)



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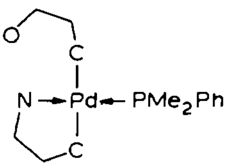
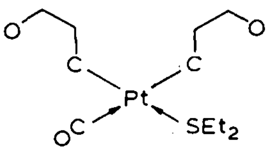
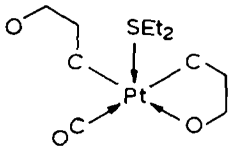


(VIa, C⌒N = B(h)q ;
VIb, C⌒N = dmna)



(VIIa)



(VIIb)

indicates that compound I exists in only one isomeric form in solution, but we cannot decide whether we are dealing with the *cis* or the *trans* isomer. Compound I is not very stable in solution. It readily gives metallic Pd and the organic dimer $(MXN)_2$ resulting from the C–C coupling reaction between two Pd bonded MXN moieties. We have characterized it by its mass and ^{1}H NMR (δ(OMe) 3.01 ppm in $CDCl_3$) spectra.

The complex *trans*-$PtCl_2(SEt_2)_2$ also reacts with "MXNLi" to give a mixture of yellow (IIa) and white (IIb) crystals, which can be separated by fractional crystallisation. These compounds have very similar IR spectra and give identical analyses, which suggest the formula $Pt(MXN)_2SEt_2$ for both IIa and IIb. The two species are therefore *cis* and *trans* isomers. Compound IIb isomerizes to IIa within a few days in a toluene solution. This isomerization is even faster in a $CDCl_3$ solution, so that we could only record the ^{1}H NMR spectrum of compound IIa. We believe that IIa is in fact the *cis* isomer because it has been reported that with the related bicyclic compounds of platinum with *N,N*-dimethylbenzylamine-2-*C,N* the *trans* isomer isomerizes to give the *cis* at high temperature [6].

The ^{1}H NMR spectrum of IIa taken at room temperature shows very broad signals for the methyl of the methoxy groups, together with the expected signals for the ethyl groups of the SEt_2 ligand. The signals of the methoxy moieties sharpen markedly at low temperature (see Experimental). One oxygen atom of the methoxy group is coordinated to the platinum (signal at 4.43 ppm with Pt satellites ^3J(Pt–H)

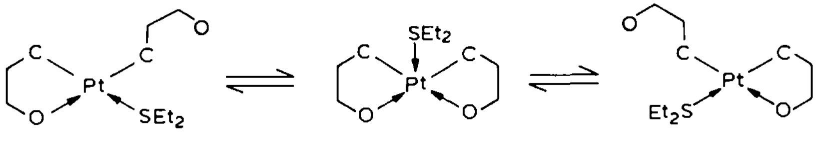
TABLE I

COMPARISON OF THE CHEMICAL SHIFTS[a] OF THE METHOXY PROTONS FOR O,C-CHELATED AND NON-CHELATED (C-BONDED) MXN LIGANDS

	MXNH	I	IIa[b]	IIIa	IIIb	IIIc	IV	V	VIa	VIb	VII
Chelated		4.44	4.43	4.43	4.49 4.42	4.48 4.41	–	–	–	–	4.74
Non chelated	3.99	–	3.70	–	–	–	3.65	3.97 (*cis*) 4.12[c] (*trans*)	3.64	3.87	3.75 4.15[c]

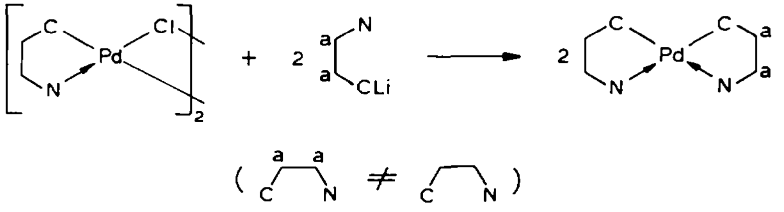
[a] In $CDCl_3$ solution unless otherwise stated. [b] In CD_2Cl_2 at −50°C. [c] These values may indicate that there is some interaction between the Pt and the OMe moiety.

~ 4 Hz) whereas the second methoxynaphthalene moiety is only bound to platinum via the 8-carbon atom of the ring (its MeO protons show a resonance at 3.7 ppm). The temperature dependence of the ^1H NMR spectrum can easily be explained by the fact that IIa is non rigid in solution. The dynamic behaviour of the molecule is due to a rapid coordination of the free MeO group and decoordination of the Pt bonded OMe group via participation of the SEt_2 moiety as in eq. 1.



(1)

We have previously shown that organometallic bicyclic compounds of palladium can be obtained by treatment of a lithiated nitrogen containing ligand with cyclopalladated dimers according to eq. 2 [3a].



(2)

These species react in an interesting way with alkynes like hexafluorobut-2-yne or bis(dimethylcarboxylate)acetylene, giving products in which the alkyne moiety has inserted in one or both Pd–C bonds to produce bicyclic compounds with one or two seven-membered ring attached to the metal. Thus the reaction of an excess of "MXNLi" and $[\{Pd(8\text{-mq})Cl\}_2]$ (8-mq = 8-methylquinoline-*C*,*N*) affords a crystalline compound IIIa. Its analytical and spectroscopic data suggest that one methoxynaphthalene moiety is bound per palladium atom. Particularly revealing is the ^1H NMR spectrum which shows the presence of the methoxy protons at 4.43 ppm and the CH_2 protons at 3.71 ppm. These data point to the presence of a single planar isomer. In order to determine unambiguously whether we are dealing with the *cis* or the *trans* isomer, and to ascertain the geometry of the new C∩O chelate we determined the molecular structure of IIIa by X-ray diffraction.

A view of the molecule and the numbering scheme used is shown in Fig. 1, and the crystal data are given in Table 2.

Interatomic distances and angles are given in Table 3 and least squares planes in Table 4.

It is at once evident that the methoxynaphthalene is bound to the palladium atom via a lone pair of the oxygen of the methoxy group and the 8-carbon of the naphthalene ring. The two C–Pd bonds are *cis* to each other: thus the harder atoms (i.e. O and N) are both *trans* to the softer ones. The Pd–C bond distances (2.002(7) and 1.986(5) Å) are not significantly different from each other, and are close to the values found for Pd–C bonds *trans* to hard ligands [7–10]. The Pd–N bond distance (2.127(6) Å) is comparable to Pd–N bond distances in molecules containing the Pd(8-mq) moiety in which the nitrogen atom is located *trans* to a ligand of high *trans* influence such as a phosphine ligand or a σ bonded carbon [12].

The Pd–O bond distance (2.236(4) Å) is much larger than that found in

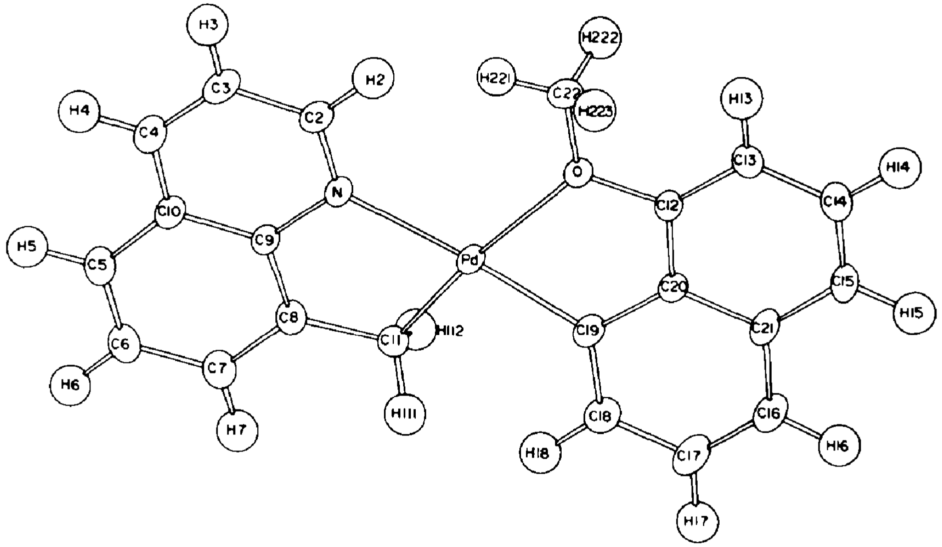
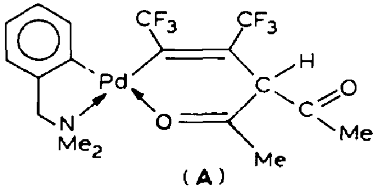


Fig. 1. ORTEP drawing of compound IIIa.

compound A [7] where the O → Pd bond length is 2.163 Å. This difference might be



(A)

due to the larger *trans* influence of the CH_2 group in IIIa compared to that of the aromatic carbon of the compound just mentioned. However, it may reflect weakness of the Pd–O compared to the Pd-N bond.

The molecule is roughly planar as illustrated by the least squares plane in Table 4, and the torsion angles between the best planes of the two palladocyclic rings are rather small ($\leqslant 7°$). The bite angle O–Pd–C(19) (79.0(2)°) and N–Pd–C(11) (82.8(2)°) are comparable to those found for related metallocyclic molecules [7–13]. The geometry of the 8-mq chelate agrees well with that in other palladium complexes containing this ligand [12].

The 1-methoxynaphthalene-8-lithium compound reacts also clearly with two other cyclopalladated dimers, viz. $[\{Pd(Bhq)Cl\}]_2$ and $[\{Pd(dmna)Cl\}_2]$ (Bhq = benzo[*h*]quinoline-9-*C*,*N*; dmna = *N*,*N*-dimethyl-1-naphthylamine-8-*C*,*N*), to give good yields of compounds IIIb and IIIc, respectively. The behaviour of these two compounds in chlorinated solvents is, however, markedly different from that of compound IIIa; thus: (i) They are not as stable as IIIa since they start to decompose slowly upon dissolution giving 1-methoxynaphthalene and the cyclopalladated dimers; thus their ^1H NMR spectra always show the presence of these two compounds together with the spectrum of IIIb or IIIc (ii) The methoxy protons

TABLE 2

SUMMARY OF CRYSTAL AND INTENSITY COLLECTION DATA FOR COMPOUND IIIa

Formula	$C_{21}H_{17}NOPd$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.901(3)
b (Å)	7.243(3)
c (Å)	16.903(3)
β	111.84(2)°
V(Å^3)	1579(1)
M	405.4
Z	4
D_c (g cm^{-3})	1.707
Crystal dimensions	0.15×0.1×0.09 mm
λ(Mo-K_α) (Å)	0.7107
μ (mm^{-1})	1.06
Scan range, deg	$1+0.142 \text{ tg } \theta$
2θ limits, deg	0–46
Reflections, total	2164
$I/\sigma(I) > 3\sigma$	1448
$R = \Sigma(\lvert F_0\rvert - \lvert F_c\rvert)/\Sigma\lvert F_0\rvert$	0.029

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATION IN PARENTHESES

Pd-O	2.236(4)	Pd-N	2.127(6)
Pd-C(11)	2.002(7)	Pd-C(19)	1.986(5)
N-C(2)	1.317(7)	N-C(9)	1.380(9)
C(2)-C(3)	1.416(9)	C(3)-C(4)	1.328(11)
C(4)-C(10)	1.395(8)	C(5)-C(10)	1.402(12)
C(5)-C(6)	1.367(10)	C(6)-C(7)	1.397(9)
C(7)-C(8)	1.391(11)	C(8)-C(9)	1.397(7)
C(8)-C(11)	1.491(8)	C(9)-C(10)	1.408(8)
O-C(12)	1.365(6)	O-C(22)	1.436(6)
C(12)-C(13)	1.372(10)	C(12)-C(20)	1.419(8)
C(13)-C(14)	1.407(9)	C(14)-C(15)	1.365(10)
C(15)-C(21)	1.397(11)	C(16)-C(21)	1.410(9)
C(16)-C(17)	1.341(11)	C(17)-C(18)	1.401(9)
C(18)-C(19)	1.378(8)	C(19)-C(20)	1.418(10)
C(20)-C(21)	1.421(7)		
O-Pd-N	105.7(2)	O-Pd-C(11)	170.2(2)
O-Pd-C(19)	79.0(2)	N-Pd-C(11)	82.8(2)
N-Pd-C(19)	175.3(2)	C(11)-Pd-C(19)	92.5(3)
Pd-O-C(12)	111.9(3)	Pd-O-C(22)	130.0(4)
Pd-N-C(2)	130.7(5)	Pd-N-C(9)	111.5(3)
Pd-C(11)-C(8)	109.7(4)	Pd-C(19)-C(18)	130.1(5)
Pd-C(19)-C(20)	114.4(4)	C(12)-O-C(22)	118.1(5)
O-C(12)-C(13)	123.4(5)	O-C(12)-C(20)	113.7(6)
C(2)-N-C(9)	117.7(5)	N-C(2)-C(3)	122.7(7)
N-C(9)-C(8)	116.2(5)	N-C(9)-C(10)	121.5(5)

Mean C-C-C of the quinoline ring 120.3(5)
Mean C-C-C of the naphthalene ring 120.2(5)

TABLE 4

LEAST SQUARES PLANES FOR COMPOUND IIIa

Plane	Atoms	Distance from plane (Å)	Plane	Atoms	Distance from plane (Å)
1	Pd	0.000	2	Pd	0.000
	N	0.000		O	0.000
	C(11)	0.000		C(19)	0.000
3	N	−0.015	4	C(12)	−0.020
	C(2)	−0.008		C(13)	−0.036
	C(3)	0.000		C(14)	−0.003
	C(4)	0.002		C(15)	0.022
	C(5)	0.002		C(16)	−0.006
	C(6)	−0.019		C(17)	−0.038
	C(7)	−0.005		C(18)	−0.018
	C(8)	0.018		C(19)	0.041
	C(9)	0.011		C(20)	0.029
	C(10)	0.014		C(21)	0.029
	C(11)[a]	0.038		O[a]	−0.075
	Pd[a]	−0.196		Pd[a]	0.097

Dihedral angles between the planes

Plane	Angle, deg.	Plane	Angle, deg.
1-2	5.1	2-4	4.5
1-3	7.9	3-4	4.2

Equations of the planes of the form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.0354	−0.9723	−0.2310	−3.5381
2	0.0818	−0.9496	−0.3025	−3.7764
3	0.1639	−0.9482	−0.2722	−3.0580
4	0.1469	−0.9289	−0.3401	−3.8193

[a] This atom was not used in defining the plane.

resonances consist of two peaks, at ca. δ 4.5 and 4.4 ppm, in a ratio which depends on the solvent used (it is 1/1 in $CDCl_3$ and 1/3 in CD_2Cl_2), and so it is obvious that IIIb and IIIc exist as mixtures of *cis* and *trans* isomers. The solvent dependance of the isomer ratio can be attributed to rapid interconversion in solution.

It is noteworthy that for all the methoxy groups bound to palladium or platinum in I–III the ^1H NMR resonances of the methyl protons are close to δ 4.5 ppm, indicating that coordination of the oxygen atom to the metal results in a low field shift of ca. 0.5 ppm for these protons. Table 1 summarizes the values of the chemical shifts of the methoxy protons in all the compounds described in this paper. It is clear from this table that there are two classes of methoxy groups, one involving metal-coordinated groups ($\delta \geqslant 4.4$ ppm), the other groups which are not interacting with the metals ($\delta < 4$ ppm).

Reactions of the metallocycles with nucleophiles

In marked contrast to the previously described bicyclic compounds of palladium involving nitrogen-containing ligands which did not react with phosphines [13], treatment of I with an excess of dimethylphenylphosphine affords compound IV in which two phosphine ligands are bound per palladium atom. Its ^{1}H NMR spectrum shows a single resonance at δ 3.65 ppm for the methoxy group, whereas the methyls of the phosphine appear as two pseudo-triplets at δ 0.86 and 0.94 ppm. These data indicate that: (i) the two phosphines are *trans* to each other [14], (ii) the two methyl groups of the phosphines are not isochronous because of the absence of a plane of symmetry for the molecule [15], and (iii) there is no interaction between the oxygen lone pairs and the palladium, the methoxy groups being in the apical sites of the molecule in a non-bonding position.

Compound IIa with the same phosphine gives a good yield of compound V, in which the methoxy resonance are at δ 3.97 ppm, again indicating that there is no interaction with the metal. The methyls of the PMe_2Ph ligand give two doublets with Pt satellites, typical of a *cis* geometry [14]. Compound V isomerizes slowly in a $CDCl_3$ into the *trans* isomer, which was characterized by its ^{1}H NMR spectrum.

Compound IIIa did not give any identifiable organometallic compound after reaction with phosphine ligands. This may be due to the fact that in this case a phosphine would have to be bonded *trans* to the CH_2 group of the 8-mq chelate, and we have shown that this is very unlikely in the case of Pd compounds [12].

In contrast, IIIb and IIIc react with an excess of PMe_2Ph to give compounds VIa and VIb, respectively. Only one phosphine ligand is bound to the palladium atom and it has displaced the O→Pd bond (δ(OMe) 3.64 (VIa) and 3.87 (VIb) ppm); this results in the absence of a plane of symmetry for these compounds (two signals are found for the methyls of PMe_2Ph). Surprisingly in the case of VIb in which the C∩N chelate is the dmna ligand, the two *N*-methyl groups give a single peak, and neither the ^4J(PH) coupling nor non-equivalence of the methyl groups can be detected. This may reflect an unusual weakness of the N→Pd bond, which is now very easily broken by the oxygen of the methoxy group, or by a slight excess of phosphine, or by any other nucleophile which is present as an impurity in the NMR solution.

Compound I reacts with carbon monoxide to give immediately and quantitatively the organic dimer $(MXN)_2$ and metallic palladium. When CO is bubbled into a toluene solution of IIIc, metallic palladium separates almost immediately. Surprisingly $(MXN)_2$ can again be isolated. No product resulting from the reaction between C∩N chelate and the MXN moiety could be detected. This is in marked contrast to the reported reaction of RLi with $[\{Pd(C\cap N)Cl\}_2]$, which gives coupling products of the form (R–C∩N) [16].

The platinum-containing compound IIa reacts with carbon monoxide to give a high yield of stable adduct VII in which one CO is bound to the platinum atom. The ^{1}H NMR spectrum at room temperature shows the presence of two sets of signals one for the MXN and the other for the SEt_2 ligands. The signals of the methoxy protons consist of three peaks in intensity ratio of 1/2/1. This can be explained by the fact that VII is a mixture of two isomers in a 1/1 ratio at room temperature. One of them, VIIa, is a compound in which neither of the two MeO groups is bonded to platinum (4.15 ppm), whereas in the other isomer VIIb, one MeO is coordinated to Pt (4.74 ppm) and the second is free (3.73 ppm). In this latter compound the SEt_2 must be in the apical position of a square pyramid. The infrared spectrum shows only a single absorption at 2030 cm^{-1} (KBr) or 2052 cm^{-1} ($CHCl_3$ solution), indicating that the CO has the same ligand *trans* to it in both isomers of VII. The ^{13}C NMR spectrum of VII with enriched ^{13}CO shows the expected two resonances for the carbonyl carbon with a large $^1J(Pt-C)$ coupling constant (~ 1120 Hz). However, these signals are not present in a 1/1 but in a 5/1 ratio, suggesting that one isomer is more stable than the other. This was confirmed by ^1H NMR spectroscopy at lower temperature: at −40°C in $CDCl_3$ the spectrum shows only the 4.15 ppm signal for OMe and the resonances at δ 2.7 and 1.32 ppm for SEt_2. Thus VIIa seems to be the more thermodynamically stable isomer.

Conclusion

We have shown in this work that metal–carbon σ bonds can be stabilized by formation of a five-membered ring through coordination to the metal of the oxygen atom of an ether function, but the oxygen → metal bond is indeed very weak. Thus the metal–carbon bonds are much less stabilized than those of corresponding compounds in which nitrogen or phosphorus ligands are bound to metal. This feature should provide molecules displaying enhanced reactivity of their metal–carbon bonds.

Experimental

The compounds $M(SEt_2)_2Cl_2$ (M = Pd, Pt) [17,18], $[\{Pd(8\text{-}mq)Cl\}_2]$ [19], $[\{Pd(dmna)Cl\}_2]$ [20] and $[\{Pd(Bhq)Cl\}_2]$ [21] were prepared by literature methods. The syntheses were performed using Schlenk tube techniques under nitrogen. All solvents were dried and distilled under N_2 prior to use. The infrared spectra were recorded as KBr pellets with a Perkin–Elmer 398 spectrophotometer. The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ spectra were recorded at 200.00, 50.32, and 80.01 MHz, respectively, on a Bruker SY 200 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. Elemental analyses were performed by the Service de Microanalyses du CNRS.

Lithiation of 1-methoxynaphtalene ("MXNLi")

A mixture of 52 ml of n-BuLi in hexane (1.6 *M*, 83 mmol) and 45 ml of Et_2O is added to a solution of 1-methoxynaphthalene (9 g, 57 mmol) in 20 ml of Et_2O. The mixture is heated under reflux for 14 h after which time a light green precipitate has formed. This is filtered off, washed with n-pentane, and dried in vacuo (2.92 g, 31%).

$Pd(MXN)_2$, bis(1-methoxynaphtalene-8-C,N)palladium(II) (I)

A deep green solution of "MXNLi" (0.49 g, 3 mmol) in 60 ml of freshly distilled THF is slowly added to a solution of $Pd(SEt_2)_2Cl_2$ (0.36 g, 1 mmol) in 15 ml THF at −78°C. The cooling bath is then removed and the mixture slowly heated to ca. 0°C. The solution is passed through a short column of alumina (5 cm × 5 cm^2) previously carefully washed with 50 ml of THF and dried in vacuo. The volume of the solution is then reduced in vacuo to 20 ml. Addition of 80 ml of n-pentane affords white crystals of I (0.22 g, 52%). Anal.: Found: C, 62.8; H, 4.3. $C_{22}H_{18}O_2Pd$ calcd.: C, 62.55; H, 4.35%. ^1H NMR ($CDCl_3$): δ 7.83–6.91 (m, 6H, aromatic protons) and 4.44 ppm (s, 3H, OCH_3).

Due to the low stability in solution the ^{13}C spectrum was not recorded.

cis and trans-Pt(MXN)$_2$(SEt$_2$): (1-methoxynaphthalene-8-C,O)- and (1-methoxynaphthalene-8-C)(diethylsulfide)platinum(II) (IIa and IIb)

A solution of "MXNLi" (0.95 g, 5.8 mmol) in 80 ml of THF is added to a solution of *trans*-Pt(SEt$_2$)$_2$Cl$_2$ (0.74 g, 1.9 mmol) in 20 ml of THF at 0°C. After 0.1 h stirring the volume of the solution is reduced to 30 ml in vacuo and 100 ml of n-pentane are added. Fractional crystallisation of this mixture at -20°C gives yellow and white crystals of IIa and IIb respectively (IIa: 0.491 g, 43%; IIb: 0.137 g, 13%). Anal.: Found: C, 52.1; H, 4.65. $C_{26}H_{28}O_2SPt$ calcd.: C, 52.05; H, 4.65%. IIa: ^{1}H NMR (CDCl$_3$, 20°C): δ 7.43–6.78 (m, 12H, aromatic protons), 4.42 (s broad, 3H, OCH$_3$), 3.64 (s broad, 3H, OCH$_3$), 2.99 (q, 4H, CH$_2$ of SEt$_2$) and 1.30 ppm (t, 6H, CH$_3$ of SEt$_2$, ^3J(HH) 7.4 Hz). (CD$_2$Cl$_2$, -40°C); δ 0.01–6.1 (m, 12H, aromatic protons), 4.43 (s, 3H, OCH$_3$, ^3J(Pt–H) ~ 4), 3.70 (s, 3H, OCH$_3$), 2.31 (q broad, 4H, CH$_2$) and 1.29 ppm (t, 6H, CH$_3$, ^3J(HH) ~ 7.2 Hz).

Pd(8-mq)(MXN): (8-methylquinoline-C,N)(1-methoxynaphtalene-8-C,O)palladium(II) (IIIa)

To a well stirred suspension of [{Pd(8-mq)Cl}$_2$] (2.3 g, 4 mmol) in 30 ml of THF is added a solution of "MXNLi" (1.88 g, 12 mmol) in 80 ml of THF at 0°C. After 0.25 h, the orange solution is filtered through a short column of alumina and its volume reduced in vacuo to 40 ml. Addition of 150 ml of pentane affords yellow crystals, which are filtered off. Keeping the mother liquor at -20°C gives after 14 h a second crop of yellow crystals (combined yield: 1.4 g, 48%). Anal.: Found: C, 60.20; H, 4.15; N, 3.6. $C_{21}H_{17}NOPd$ calcd.: C, 62.15; H, 4.20; N, 3.45%. ^{1}H NMR (CDCl$_3$): δ: 8.85–6.90 (m, 12H, aromatic protons), 4.43 (s, 3H, CH$_3$) and 3.71 ppm (s, 2H, CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ 149.6, 148.0, 137.6, 130.6, 129.0, 127.5, 126.0, 123.9, 123.2, 122.6, 121.8, 120.9, 104.5 (aromatic carbons), 61.0 (CH$_3$) and 21.6 ppm (CH$_2$).

Compounds IIIb and IIIc are obtained by a procedure similar to that described for IIIa by treatment of [{Pd(Bhq)Cl}$_2$] or [{Pd(dmna)Cl}$_2$] with a two-fold excess of "MXNLi".

Pd(Bhq)(MXN): (benzo(h)quinoline-9-C,N)(1-methoxynaphtalene-8,C,O)palladium(II) (IIIb)

Anal.: Found: C, 65.15; H, 3.75; N, 3.0. $C_{24}H_{17}NOPd$ calcd.: C, 65.25; H, 3.85; N, 3.15%. ^{1}H NMR (CDCl$_3$): δ 9.02–6.86 (m, 14H, aromatic protons), 4.50 and 4.42 ppm (two s, (1/1), 3H, CH$_3$).

Pd(dmna)(MXN): (N,N-dimethyl-1-naphthylamine-8-C,N)(1-methoxynaphthalene-8-C,N)palladium(II) (IIIc)

Anal.: Found: C, 64.55; H, 5.1; N, 2.7. $C_{23}H_{21}NOPd$ calcd.: C, 63.7; N, 4.85; N, 3.25%. ^{1}H NMR (CDCl$_3$): δ 7.87–6.93 (m, 12H, aromatic protons), 4.49 and 4.41 (two s, (1/1), 3H, O–CH$_3$), 3.46 and 3.43 ppm (two s, (1/1), 6H, N(CH$_3$)$_2$).

Pd(MXN)$_2$(PMe$_2$Ph)$_2$: bis(1-methoxynaphtalene-8-C)bis(dimethylphenylphosphine)palladium(II) (IV)

Addition of an excess of PMe$_2$Ph (0.138 g, 1 mmol) to a solution of I (0.05 g, 0.12 mmol) in toluene (10 ml) gives a deep red solution. Pentane (50 ml) is added to it until the solution turns yellow. It is then kept at -20°C for 24 h, to yield yellow crystals of IV (23 mg, 28%). Anal.: Found: C, 64.6; H, 5.7. $C_{54}H_{40}O_2P_2Pd$ calcd.: C, 65.45; H, 5.75%. ^1H NMR ($CDCl_3$): δ 7.73–6.49 (m, 11H, aromatic protons), 3.65 (s, 3H, OCH_3), 0.94 and 0.87 ppm (two t, 6H, $P(CH_3)_2$, $|^4J(PH)+{}^2J(PH)| = 3.3$ Hz). ^{31}P NMR ($CDCl_3$): δ −9.3 ppm.

cis-Pt(MXN)$_2$(PMe$_2$Ph)$_2$: bis(1-methoxynaphthalene-8-C)bis(dimethylphenylphosphine)platinum(II) (V)

This compound is obtained in 65% yield by the procedure described for IV but starting with compound IIa. Anal.: Found: C, 58.2; H, 4.8. $C_{34}H_{40}O_2P_2Pt$ calcd.: C, 58.1; H, 5.1%. ^1H NMR ($CDCl_3$): δ 8.1–6.48 (m, 11H, aromatic protons), 3.76 (s, 3H, OCH_3), 0.97 (d, 3H, $P(CH_3)$, $^2J(PH)$ 8.4, $^3J(Pt\text{–}H)$ 19 Hz) and 0.85 ppm (d, 3H, $P(CH_3)$, $^2J(PH)$ 8.4, $^3J(Pt\text{–}H)$ 24 Hz). ^{31}P NMR ($CDCl_3$): δ −19.3 ppm, $^1J(Pt\text{–}P)$ 2048.5 Hz.

Compound V isomerizes slowly in solution to give the corresponding *trans* isomer with the following spectroscopic characteristics ^1H NMR ($CDCl_3$): δ 7.86–6.68 (m, 11H, aromatic protons), 4.13 (s, 3H, OCH_3) and 0.92 ppm (two overlapping triplets with Pt satelites $|^4J(PH)^+ {}^2J(PH)| \sim 4.4$ Hz). ^{31}P NMR ($CDCl_3$): δ −18.4 ppm, $^1J(Pt\text{–}P)$ 2053 Hz.

Pd(Bhq)(MXN)PMe$_2$Ph: (benzo[h]quinoline-9-C,N)(1-methoxynaphthalene-8-C)(dimethylphenylphosphine)palladium(II) (VIa)

PMe_2Ph (0.138 g, 1 mmol) is added to a yellow solution of IIIb (0.221 g, 0.5 mmol) in THF (20 ml) giving an orange solution. It is concentrated to half its volume and pentane (30 ml) is added. After 3 days at −20°C yellow crystals of VIa are obtained (0.130 g, 45%). Anal.: Found: C, 66.25; H, 4.85; N, 2.4. $C_{32}H_{28}NOPPd$ calcd.: C, 66.25; H, 4.85; N, 2.4%. ($CDCl_3$): δ 8.15–6.61 (m, 19H, aromatic protons), 3.63 (s, 3H, OCH_3), 1.26 and 1.14 ppm (two d, 6H, $P(CH_3)_2$, $^2J(PH)$ 7 Hz). ^{31}P NMR ($CDCl_3$): δ −10.7 ppm.

Pd(dmna)(MXN)PMe$_2$Ph: (N,N-dimethyl-1-naphthylamine-8-C,N)(1-methoxynaphthalene-8-C)(dimethylphenylphosphine)palladium(II) (VIb)

PMe_2Ph (0.138 g, 1 mmol) is added to a solution of IIIc (0.147 mg, 0.34 mmol) in diethyl ether (10 ml). 50 ml of n-hexane are added and the mixture is then filtered to remove a brown precipitate. After 20 h at −20°C white crystals of VIb are obtained (0.03 g, 16%). Anal.: Found: C, 64.55; H, 5.7; N, 2.3. $C_{31}H_{32}NOPPd$ calcd.: C, 65.05; H, 6.5; N, 2.15%. ^1H NMR ($CDCl_3$): δ 8.23–6.20 (m, 17H, aromatic protons), 3.87 (s, 3H, OCH_3), 3.01 (s, 6H, $N(CH_3)_2$), 1.22 and 1.02 ppm (two d, 6H, $(P(CH_3)_2$. $^2J(PH)$ 6.6 Hz). ^{31}P NMR ($CDCl_3$): δ −14.4 ppm.

Pt(MXN)$_2$(SEt$_2$)CO: bis(1-methoxynaphthalene-8-C)(diethylsulfide) (carbonyl)platinum(II) (VII)

CO is bubbled into a suspension of compound IIa (0.120 mg, 0.2 mmol) in toluene (10 ml) until the IIa has completely dissolved. Pentane (75 ml) is then added and the solution is kept at −20°C for 3 days to give well-shaped yellow crystals of VII (0.08 g, 70%). Anal.: Found: C, 51.6; H, 4.3. $C_{27}H_{28}O_3SPt$ calcd.: C, 51.65; H, 4.45%. IR $\nu(C{\equiv}O)$ (KBr pellet): 2030; ($CHCl_3$): solution 2052 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0–6.4 (m, 12H, aromatic protons), 4.74, 4.15 and 3.73 (three s, (1/2/1), 6H, OCH_3), 2.7 and 2.55 (two overlapping q, 4H, CH_2 of Et), 1.32 and

1.25 (two overlapping t, 6H, CH_3 of Et, $^3J(HH)$ 3.5 Hz). ^{13}C NMR ($CDCl_3$): 182.3 (s, CO, $^1J(Pt-C)$ 1121.5), 177.4 ppm (s, CO, $^1J(Pt-C)$ 1119 Hz).

Collection of the X-ray data and structure determination

Crystals of compound IIIa suitable for X-ray diffraction study were obtained by slow diffusion of n-pentane into a solution of IIIa in CH_2Cl_2 at −20°C.

Cell constants and other pertinent data are presented in Table 2. Intensity data were collected on a Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection periods. Absorption corrections were omitted in view of the low linear absorption coefficient. The structure was solved by direct methods [22]. Refinement by full-matrix least squares (all non hydrogen atoms anisotropic) have proceeded to the *R* factor value indicated in Table 2. Complex neutral scattering factors were used [23]. All computer calculations were performed using the SHELX Package [24]. Tables of final positional and thermal parameters for all atoms and of the observed and calculated structure factors are available from the authors.

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