EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201402954

Platinum Diolefin Complexes – Synthesis, Structures, and Cytotoxicity

Anna Lüning,[a] Michael Neugebauer,[a] Verena Lingen,[a,b] Alexander Krest,[a] Kathrin Stirnat,[a] Glen B. Deacon,[b] Penny R. Drago,[b] Ingo Ott,[c] Julia Schur,[c] Ingo Pantenburg,[a] Gerd Meyer,[a] and Axel Klein*[a]

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Keywords: Platinum / Alkene ligands / Structure elucidation / Structure–activity relationships / Cytotoxicity

The synthesis, spectroscopy, structures and chemical reactivity of platinum(II) diolefin complexes *cis*-[(II^II)$PtCl_2$], *cis*-[(II^II)PtCl(R)] and *cis*-[(II^II)$Pt(R)_2$] [II^II = chelate diolefin ligand: 1,5-cyclooctadiene (COD), 1,5-dimethylocta-1,5-diene (Me_2COD), norbornadiene (NBD), 1,5-hexadiene (HEX), 3-allyloxypropene (All_2O, diallyl ether), diallylamine (All_2NH); R = Me, Bn, C_6F_5, C_6F_4H-4 (or -5), or C≡C(4-Me)Ph] have been explored. The relative exchange rates of the *cis*-[(II^II)-$PtCl_2$] complexes towards the diimine ligand diisopropyl-1,4-diazabutadiene (*i*Pr-DAB) increased along the series COD < Me_2COD < NBD < HEX < All_2O by a factor of 4. The presumably dimeric complex $[(All_2NH)PtCl_2]_2$ undergoes a unique rearrangement process in dimethyl sulfoxide (DMSO) solution to yield the dimeric piperazine complex $[PtCl(dmso)(C_6H_{10}N)]_2$, which has been characterised by single-crystal XRD. For selected platinum complexes, cytotoxic effects in HT-29 colon carcinoma and MCF-7 breast cancer cell lines were evaluated. For comparison, the dicationic complexes $[(COD)Pt(Bn)(L)][PF_6]_2$ with the very labile coligands *N*-methyl-4,4′-bipyridinium (MQ^+) and *N*-methyl-1,4-pyrazinium (Mpz^+) were added to the study. Although the hexadiene complexes $[(HEX)Pt(C_6F_4H\text{-}4)_2]$ and $[(HEX)Pt(C_6F_4H\text{-}5)_2]$ show strong cytotoxicity, the introduction of labile diolefin ligands or the labile cationic MQ^+ or Mpz^+ coligands does not generally lead to markedly increased cytotoxicity.

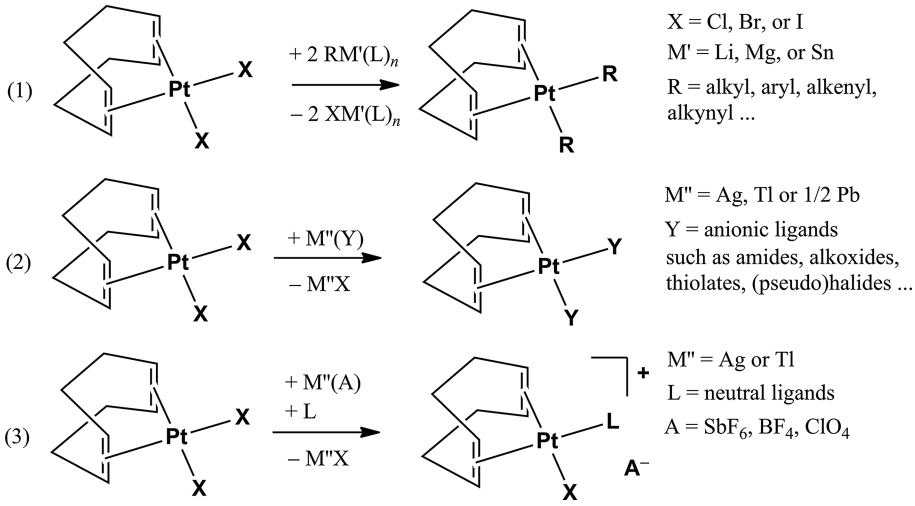
Introduction

The binding of olefins to transition metal ions reveals a marked maximum of stability for platinum(II) and palladium(II). This observation can be explained from the best match of promotion energy (should be low) and electron affinity (should be high).[1,2] Given the inert nature of Pt^{II}, it is unsurprising that Zeise prepared $K[PtCl_3(C_2H_4)]$ (Zeise's salt) in 1827, which is considered to be the first organometallic complex.[2–5] The Pd^{II} derivative $[PdCl_3(C_2H_4)]^-$ plays a crucial role in one of the most important industrial chemical processes, that is, the oxidation of ethane in the so-called Wacker–Hoechst process (also Wacker oxidation).[6]

To enhance the stability of olefin platinum complexes, the chelate effect is crucial, and 1,5-cyclooctadiene (COD) is best for this purpose. The relatively high stability of COD complexes opens several routes for the derivatisation of the frequently used starting complex $[(COD)PtCl_2]$ (Scheme 1). Firstly, the quite stable CODPt scaffold allows the replacement of one or two Cl coligands by carbanionic coligands, such as alkyl,[7–13] aryl,[10–14] alkynyl,[13–18] alkenyl[16,19] or cyclopentadienide,[20] to form various derivatives (Scheme 1, Reaction 1) or by other anionic coligands such as amides,[21] thiolates,[22,23] SCN^- or pseudohalides (Scheme 1, Reaction 2).[7,10,22,24] The limit of this reaction is set by strong nucleophiles (Nu), which attack the olefin double bond to yield a Pt–C–C–Nu unit with a Pt–C σ bond.[7,25,26] Neutral coligands can be introduced by abstraction of a Cl^- ion with Ag^+ or Tl^+ salts to yield cationic complexes (Scheme 1, Reaction 3).[13,14,26] The choice of an appropriate ligand even allows the introduction of a monoanionic chelate ligand for the two Cl^- coligands,[27] whereas reactions with neutral chelate ligands lead to the

[a] Universität zu Köln, Department für Chemie, Institut für Anorganische Chemie,
Greinstrasse 6, 50939 Köln, Germany
E-mail: axel.klein@uni-koeln.de
http://www.klein.uni-koeln.de/
[b] School of Chemistry, Monash University,
P. O. Box 23, VIC 3800, Australia
[c] Institute of Medicinal and Pharmaceutical Chemistry,
Technische Universität Braunschweig,
Beethovenstraße 55, 38106 Braunschweig, Germany

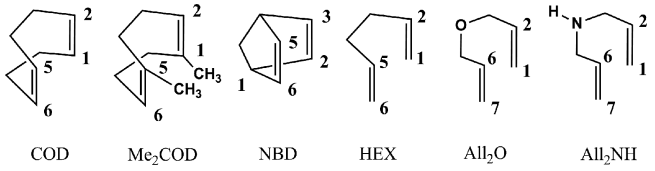
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402954.



Scheme 1. Derivatisation reactions of [(COD)PtX_2] precursor complexes.

replacement of COD (bidentate) or COD and Cl^- (polydentate ligands).[11–13,21,24,28] Today, a wealth of four-coordinate square-planar CODPt complexes are known. Most of them serve as precursor complexes in coordination chemistry[11–29] or as precursors in chemical vapour deposition (CVD) and related processes.[30,31] Both of these applications take advantage of the substitution or cleavage of the COD ligand, processes which require thermal activation.

For other diolefin ligands (||^||) such as norbornadiene (NBD), 1,5-hexadiene (HEX), diallyl ether (All_2O) and diallylamine (All_2NH; Scheme 2), essentially the same derivatisation reactions (as those shown in Scheme 1) of the corresponding [(||^||)$PtCl_2$] complexes have been reported.[12,28,32–35] However, their stability towards the exchange of the diolefin ligand with other neutral ligands is markedly lower than that with COD,[9a,12,28,29,32,33,35–38] and their markedly higher tendency for nucleophilic attack of anionic ligands on the coordinated olefin groups also renders the Pt^{II} complexes of other diolefin ligands less stable.[7,39,40]



Scheme 2. Diolefin ligands used in this study. COD = 1,5-cyclooctadiene, Me_2COD = 1,5-dimethylcycloocta-1,5-diene, NBD = norbornadiene (bicycloheptadiene), HEX = 1,5-hexadiene, All_2O = 3-allyloxypropene (diallyl ether) and All_2NH = diallylamine.

In the course of our investigations on the organometallic derivatives [(COD)$Pt(R)_2$], [(COD)Pt(R)(R′)], [(COD)$Pt(R')_2$] and [(COD)PtCl(R)] (R = alkyl; R′ = alkynyl),[13,14] we recently found that such organometallic derivatives exhibit marked cytotoxicity towards selected cancer cell lines, whereas [(COD)$PtCl_2$] is virtually nontoxic. Within the organometallic derivatives, the alkynyl complexes [(COD)Pt(R)(R′)] and [(COD)$Pt(R')_2$] (R′ = C≡C–aryl) were the most toxic.[13] Furthermore, we very recently found that the mixed alkyl alkynyl complexes [(COD)Pt(R)(R′)] undergo self-transmetallation {[(COD)Pt(R)(R′)]→[(COD)$Pt(R)_2$] + [(COD)$Pt(R')_2$]}, and the dialkynyl complexes readily decompose to COD, elemental Pt and the R′–R′ coupling product. However, the tendency to hydrolyse the Pt–R or Pt–R′ bonds is rather low.[13a] On the basis of these results, we might assume that the alkylation reaction or the formation of Pt (nano)particles is responsible for the observed toxicity. Another option might be the replacement of the COD ligand and the binding of the Pt centre to DNA, as has been well established for cisplatin and other platinum-based anticancer drugs.[41,42] For example, the replacement of ethene from the complexes [PtCl(C_2H_4)(chxn)]Cl (chxn = *R*,*R*- or *S*,*S*-1,2-diaminocyclohexane) and subsequent hydrolysis leads to the same Pt species as that observed for oxaliplatin.[43] However, the overall cytotoxicity of these ethene complexes is generally markedly lower than those of cisplatin and oxaliplatin, and they have low IC_{50} values of ca. 100 μM; thus, they are far less toxic than many of the CODPt complexes mentioned above.

As COD is not easily replaceable (usually requires thermal activation), we used less strongly bound diolefin ligands to prepare selected complexes of the type *cis*-[(||^||)$PtCl_2$], *cis*-[(||^||)PtCl(R)] or *cis*-[(||^||)$Pt(R)_2$] [(||^||) = diolefin ligands in Scheme 2, R = Me or C≡C(4-Me)Ph] and assessed the consequences of this variation on the structures, reactivity and cytotoxicity of the complexes. The results of this study are reported herein. A similar approach with the COD, NBD and HEX complexes [(||^||)Pt($C_6F_xH_y$)$_2$] ($x + y = 5$)[32a] was recently reported, and the results of that study will be compared with ours. Only very recently, Bräse et al. reported a similar approach with monosubstituted COD (R–COD).[44] The toxicities of the corresponding complexes [(R–COD)Pt(Me)(L)] (with L = Cl, I, nC_3F_7, iC_3F_7, nC_8F_{17}, Me, aryl, alkynyl and R = H, Me, Et, *i*Pr, *n*Bu, *i*Bu, *n*Hex, Ph) towards HeLa cells are in

part higher than that of cisplatin, but the observed variations in toxicity were due to differences in solubility or lipophilicity rather than to structural differences. In view of our approach, this is not unexpected, as R–COD ligands probably do not enhance the lability of the corresponding complexes compared with those of COD derivatives.

Finally, we also added the complexes [(HEX)Pt(C_6F_4H-4)$_2$], [(HEX)Pt(C_6F_4H-5)$_2$], [(COD)Pt(Ph)$_2$] and [(COD)Pt(Bn)(L)][PF_6]$_2$ with the very labile coligands *N*-methyl-4,4′-bipyridinium (MQ^+) and *N*-methyl-1,4-pyrazinium (Mpz^+) to this study. The anticancer activity of the present complexes is of particular interest, as they markedly deviate from the structure–activity rules for established platinum anticancer compounds.[41,42]

Results and Discussion

Synthesis and Analytical Characterisation

The dichlorido complexes [(||^||)PtCl$_2$] [||^|| = COD, Me_2-COD, NBD, HEX and All$_2$O (Scheme 2)] were prepared by established literature methods (see Exp. Sect.). The monomeric complex [(All$_2$NH)PtCl$_2$] could not be obtained; instead, the previously reported dimer [(All$_2$NH)-PtCl$_2$]$_2$ was identified as the yellow product of the corresponding reaction.[45] Interestingly, the recrystallisation of the material from dimethyl sulfoxide (DMSO) gave colourless crystals of the dimeric piperazine complex [PtCl(dmso)($C_6H_{10}N$)]$_2$, which has probably been formed in a unique rearrangement process (outlined in the next section).

In the next step, the olefin complexes [(||^||)PtCl$_2$] were examined in alkylation reactions with the corresponding Grignard reagents RMgX or stannanes $RSnMe_3$ (R = Me, Bn, or C_6F_5; Scheme 1). The reactions of the COD, Me_2-COD and NBD complexes yielded the desired dialkyl complexes [(||^||)Pt(R)$_2$], which could be transformed to the chlorido alkyl derivatives [(||^||)Pt(R)Cl] by reaction with in situ generated "HCl" from acetyl chloride and methanol. For the dichlorido complexes carrying HEX, All$_2$NH or All$_2$O ligands, the corresponding transmetallation reactions largely failed. Reactions with MeMgBr as the transmetallating agent led to the formation of the well-known tetrameric Pt^{IV} compound [($PtMe_3$)$_4\mu^3$-Br$_4$][46] and only small amounts of [(||^||)Pt(Me)Br] (details in the Exp. Sect.). The corresponding reactions with MeLi, BnMgBr and $BnSnMe_3$ led to black, decomposed material. Presumably, during the attempted alkylation of the platinum atom (transmetallation), nucleophilic attack at the olefin sites occurs, and the resulting species decompose during workup. Test reactions were performed in NMR tubes at low temperatures, and the appearance of Pt satellites (^{195}Pt, *I* = 1/2; natural abundance 33.8%) for the corresponding alkyl moieties revealed only very small amounts of transmetallation products in these cases. Furthermore, the complex [(HEX)Pt(Me)Br], which could be prepared in sizeable amounts, is fragile in solution and forms [($PtMe_3$)$_4\mu_3$-Br$_4$]. In contrast, the reaction of [(HEX)PtCl$_2$] with Li(C_6F_4H-5) (from 1-bromo-2,3,4,6-tetrafluorobenzene and *n*BuLi) gave [(HEX)Pt(C_6F_4H-5)$_2$] in good yield. The derivative [(HEX)-Pt(C_6F_4H-4)$_2$] has been prepared previously.[32c] Clearly, arylation reactions with fluoroaryl groups are less endangered by side-reactions, and the products are far more stable. The chlorido complexes [(||^||)PtCl$_2$] and [(||^||)Pt(R)Cl] (||^|| = COD, Me_2COD, NBD) were treated with HC≡C(4-Me)Ph in the presence of base to afford the alkynyl complexes [(||^||)Pt(C≡C(4-Me)Ph)$_2$] and [(||^||)Pt(R)(C≡C(4-Me)Ph)] (R = Me or Bn). These reactions were only successful for COD and Me_2COD; for the NBD derivatives, no isolable products could be identified in the blackish precipitate obtained.

Crystal and Molecular Structures

Single crystals of the compounds [(Me_2COD)PtCl$_2$], [(Me_2COD)Pt(C_6F_5)$_2$], [(HEX)PtCl$_2$] and [PtCl(dmso)-($C_6H_{10}N$)]$_2$ were obtained, and X-ray diffraction data sets were collected. The complexes [(Me_2COD)Pt(C_6F_5)$_2$], [(HEX)PtCl$_2$] and [PtCl(dmso)($C_6H_{10}N$)]$_2$ crystallise in the monoclinic space groups *C*2/*c*, $P2_1/n$ and $P2_1/c$, respectively. The structure of [(Me_2COD)PtCl$_2$] was solved in the orthorhombic space group *Ccmm*. Owing to the high symmetry, all olefinic C atoms are identical, and each contains a CH_3 group. This disorder could not be modelled satisfactorily, although the measurements were performed at 100(2) K for this complex. Attempts to lower the symmetry to enable a structure solution failed (for details, see Exp. Sect.). The important structural parameters are listed in Table 1 (full structural information in the Supporting Information), and Figures 1–3 show representative examples of the crystal and molecular structures.

In the crystal structures of [(Me_2COD)Pt(C_6F_5)$_2$], [(Me_2-COD)PtCl$_2$] and [(HEX)PtCl$_2$], multiple intermolecular interactions contribute to the crystal packing. In all three complexes, weak hydrogen bridges were observed, and π–π stacking is found in [(Me_2COD)Pt(C_6F_5)$_2$] (data in Supporting Information). The corresponding molecules show almost ideal square-planar geometries when a central binding position (centroid) between the two olefin C atoms is assumed for the olefin ligands.

In the crystal structure of [(dmso)PtCl($C_6H_{10}N$)]$_2$ (Figure 3), there are weak intermolecular hydrogen bridging C–H···O interactions ranging from 2.650(5) to 2.823(8) Å as well as short C–H···Cl contacts of more than 2.8 Å (see Supporting Information). The molecular structure reveals two perfectly square-planar-coordinated Pt^{II} atoms in an eight-membered (Pt–N–C–C)$_2$ metallacycle. Clearly, the starting dinuclear complex [(AllNH)PtCl$_2$]$_2$ has undergone a transformation that probably starts with the replacement of one of the Cl coligands on each Pt atom by a DMSO molecule and subsequent deprotonation of the NH function (of the cationic complex species). This is followed by a nucleophilic attack of the N atom at the *β*-allyl C atom and a metallation of the C-*α* atom (Scheme 3). Combined with an exchange of the N coordination sites, the latter reaction

Table 1. Crystal structure measurement and refinement parameters for [(Me_2COD)$PtCl_2$], [(Me_2COD)Pt(C_6F_5)$_2$], [(HEX)$PtCl_2$] and [(dmso)PtCl($C_6H_{10}N$)]$_2$.[a]

	[(Me_2COD)$PtCl_2$][b]	[(Me_2COD)Pt(C_6F_5)$_2$]	[(HEX)$PtCl_2$]	[(dmso)PtCl($C_6H_{10}N$)]$_2$
Formula	$C_{10}H_{16}C_{12}Pt$	$C_{22}H_{16}F_{10}Pt$	$C_6H_{10}Cl_2Pt$	$C_{16}H_{32}Cl_2N_2O_2Pt_2S_2$
Weight [g/mol]	402.22	665.44	348.13	809.64
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Ccmm*	*C*2/*c*	$P2_1/n$	$P2_1/c$
a [Å]	7.753(1)	14.238(2)	9.184(1), 8.170(1), 11.661(2)	10.9783(5)
b [Å]	13.100(2)	8.512(1)	90	10.1147(4)
c [Å]	11.015(3)	18.587(3)	105.95(1)	11.7519(7)
α [°]	90	90	90	90
β [°]	90	112.26(1)		118.942(4)
γ [°]	90	90		90
V [Å^3]/*Z*	1118.7(3)/4	2084.7(6)/4	841.3(2)/4	1141.9(1)/2
$\rho_{calcd.}$ [g/cm^3]	2.388	2.120	2.748	2.355
μ [mm^{-1}]	12.972	6.826	17.226	12.667
Limiting indices	$-9 < h < 9$, $-16 < k < 16$, $-14 < l < 14$	$-18 < h < 17$, $-10 < k < 10$, $-23 < l < 23$	$-12 < h < 12$, $-10 < k < 11$, $-16 < l < 16$	$-15 < h < 15$, $-13 < k < 13$, $-14 < l < 16$
Reflections collected/unique	6225/683	15912/2336	12855/2331	14660/3091
R_{int}	0.0850	0.01168	0.0539	0.0717
Data/restraints/parameters	683/0/39	2336/0/151	2331/0/83	3067/0/125
Goof on F^2	1.258	0.915	1.052	1.062
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0321, 0.0952	0.0410, 0.0737	0.0247, 0.0523	0.0325, 0.0727
R_1, wR_2 (all data)	0.0335, 0.0959	0.0906, 0.0873	0.0361, 0.0576	0.0466, 0.0789
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.745/1.189	–2.465/1.006	–0.941/1.413	–1.869/1.819
Distances [Å]				
Pt–Cl	2.327(3), 2.327(3)		2.299(2), 2.300(2)	2.414(2)
Pt–C	2.171(1), 2.171(1), 2.171(1), 2.171(1)	2.021(9), 2.021(9)	2.151(6), 2.153(7), 2.277(6), 2.178(5)	2.054(5)
Pt–X [c]	2.067(4), 2.067(4)	2.176(5), 2.176(5)	2.051(3), 2.049(3)	–
Pt–S	–	–	–	2.186(2)
Pt–N	–	–	–	2.127(5)
Angles [°]				
C–Pt–X [c]	72.2(8)	93.7(3), 93.7(3)	72.3(6), 70.3(5), 70.2(5), 72.3(6)	–
C–Pt–C	72.2(6)	87.7(3)	72.3(5), 72.3(4)	–
X–Pt–X [c]	87.2(1)	85.8(2)	91.6(7)	–
X–Pt–Cl [c]	93.0(1), 93.0(1)		88.8(4), 90.2(4)	–
Cl–Pt–Cl	86.8(1)		89.4(6)	–
C–Pt–N	–	–	–	83.5(2)
C–Pt–S	–	–	–	91.6(2)
N–Pt–Cl	–	–	–	92.8(1)
S–Pt–Cl	–	–	–	91.94(6)
Sum of Pt angles	360.0(1)	360.9(3)	360.0(5)	359.9(2)

[a] Radiation wavelength λ = 0.71073 Å; T = 293(2) K; refinement method: full-matrix least-squares on F^2. [b] Measured at T = 100(2) K. [c] X = centroids of the C=C bond.

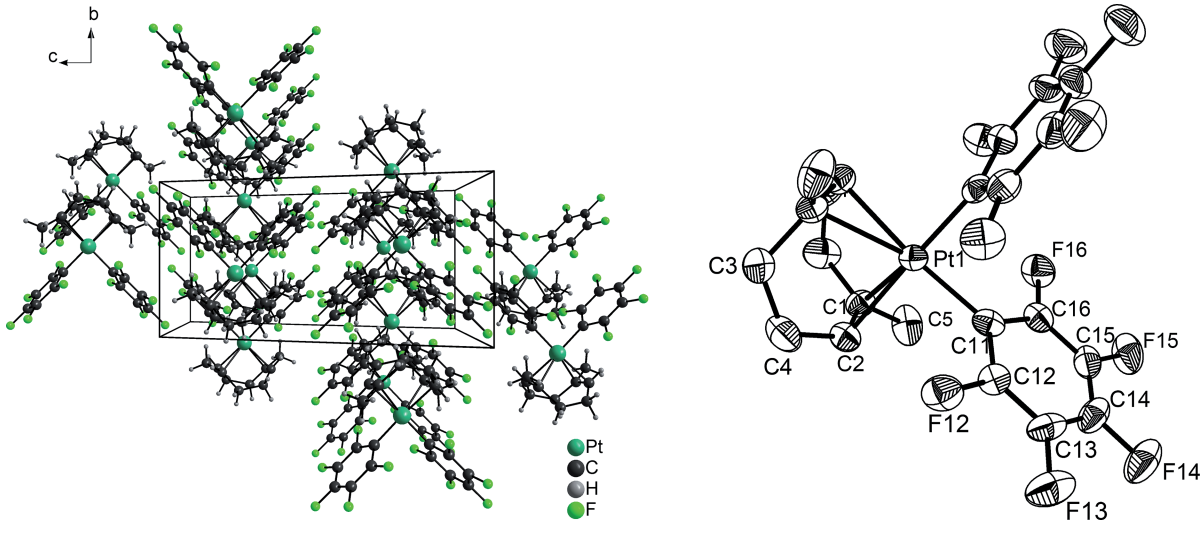


Figure 1. Left: crystal structure of [(Me_2COD)Pt(C_6F_5)$_2$] showing π–π interactions. Right: molecular structure of [(Me_2COD)Pt-(C_6F_5)$_2$] with atoms at 50% probability level; hydrogen atoms are omitted for clarity.

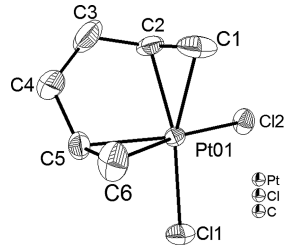


Figure 2. Molecular structure of [(HEX)$PtCl_2$] with atoms at 50% probability level; hydrogen atoms are omitted for clarity.

leads to two five-membered Pt–N–C–C–CH_2 rings, which are both part of a central piperazine core in an unprecedented bridging (1,4-diallylpiperazine-2,5-diyl)dimethanide ligand. The second allyl N function remains intact but does not coordinate to the Pt^{II} centre. Without a N ligand rearrangement, the nucleophilic attack and C metallation would lead to a species with four-membered metallacycles (intermediate in Scheme 3). However, we do not have any evidence for such a species. A closer look at Scheme 3 also reveals that the assumption of Denning and Venanzi[45] that [(AllNH)$PtCl_2$]$_2$ exhibits a *trans* stereochemistry around the Pt atoms (Scheme 3, bottom left) is probably not correct. From our proposed mechanism, the nucleophilic N atom and the coordinated olefin need to be in a *cis* position.

There are only two comparable structures in the Cambridge Crystallographic Database (accessed Jan 20, 2014), namely, the quite similar dinuclear platinapyrrolidine complex [(PEt_3)ClPt(Me_2NCH_2CH–)$_2$][47] and the bis-platinated ferrocene [Fe($C_5H_3CH_2NMe_2PtCl$(dmso))$_2$].[48] In the latter, the dmso ligand binds through the S atom, and the bond parameters around the Pt atom are quite similar in all three complexes.

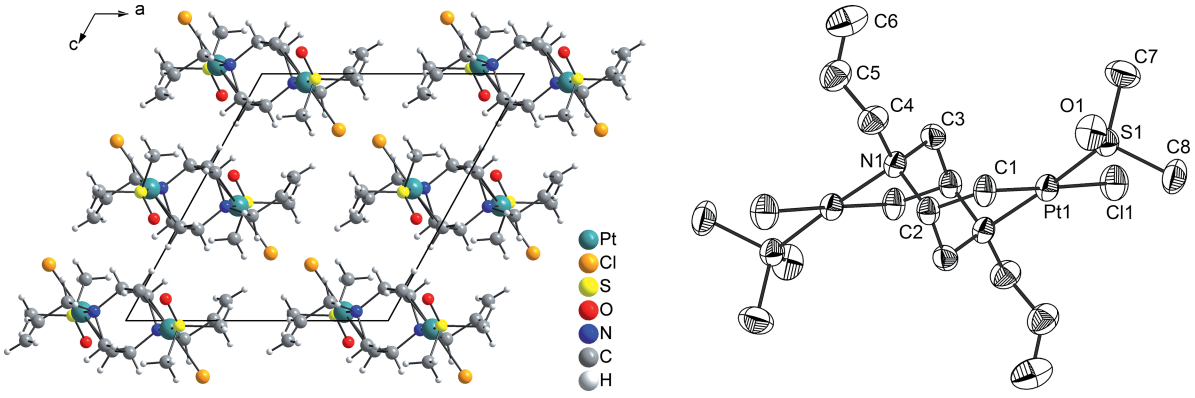
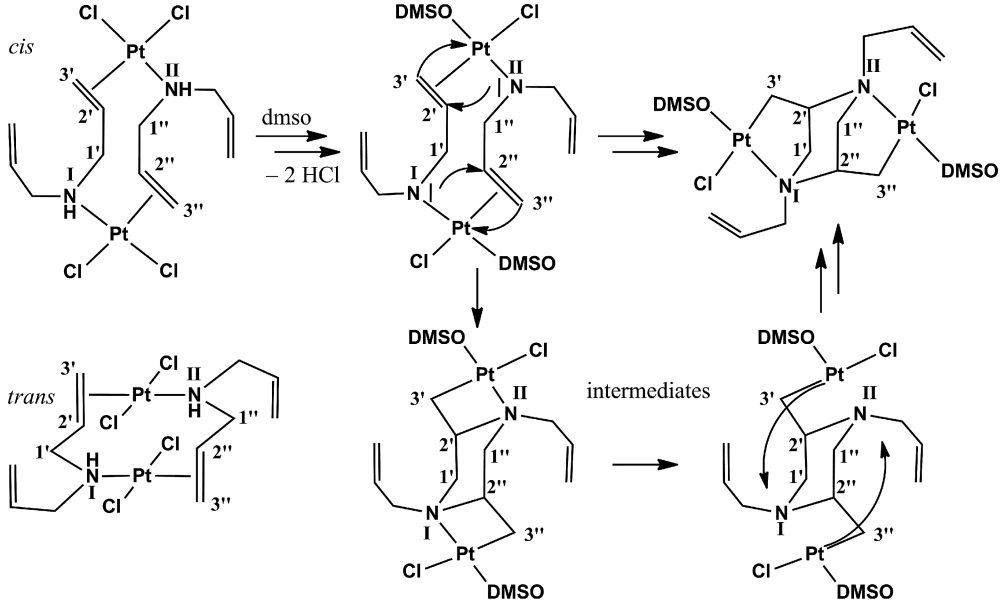


Figure 3. Left: crystal structure of [(dmso)PtCl($C_6H_{10}N_2$)]$_2$ viewed along the *b* axis. Right: molecular structure with atoms at 50% probability level; hydrogen atoms are omitted for clarity.



Scheme 3. Proposed reaction scheme for the formation of [(dmso)PtCl($C_6H_{10}N$)]$_2$ from [(All_2NH)$PtCl_2$]$_2$ (both forms proposed by Denning and Venanzi[45] are shown) in DMSO solution.

NMR Spectroscopy and Bond (Ligand) Strength

All new complexes were thoroughly characterised by multinuclear NMR spectroscopy, and the results are compiled in Table 2. From previous studies,[13,14] the $^2J_{Pt,H(=CH)}$ coupling constants reflect very well the general Pt–ligand bond strength of a ligand *trans* to the corresponding olefin proton. Also, other $^nJ_{Pt,X}$ coupling constants have been very successfully correlated with the strength of *trans* Pt–ligand bonds.[42,49,50] As shown in Table 2, the $^2J_{Pt,CH_3}$ coupling constants for the dimethyl complexes are almost identical for COD (83 Hz) and Me_2COD (82 Hz) and markedly higher for NBD (91 Hz); for the [Pt(Me)Cl] complexes, the same trend is found, and the values for Me_2COD (74 Hz) and COD (73 Hz) are again very similar. This indicates that Me_2COD exerts a very similar *trans* influence to that of COD, and both show a markedly stronger influence compared with that of NBD. We conclude from this that the methyl substituents might render Me_2COD a slightly stronger σ donor but at the same time a weaker π acceptor compared with COD, and the two effects cancel each other. For [(HEX)Pt(Me)Br], the $^2J_{Pt,CH_3}$ coupling constant of 72 Hz indicates that the HEX ligand has quite a strong *trans* influence.

On the other hand, the $^2J_{Pt,H(=CH)}$ values for the series of chlorido complexes drop from ca. 68 Hz for NBD and COD to 63 Hz for Me_2COD and ca. 61 Hz for HEX and All_2O; these values indicate a slightly weaker bonding for the last three olefin ligands. The same trend can be observed for the dimethyl complexes of NBD (40 Hz), COD (42 Hz) and Me_2COD (36 Hz), whereas no clear trend can be observed for the [Pt(Me)Cl] complexes. Also, although the dichlorido complex of the HEX ligand shows a markedly smaller coupling constant than those of the COD or NBD derivatives, the HEX ligand in the methyl bromido complex [(HEX)Pt(Me)Br] seems to bind as strongly as the COD and NBD ligands in the corresponding methyl chlorido complexes. Thus, from the $^2J_{Pt,H(=CH)}$ values, we cannot draw a conclusive series for the Pt–||^|| bond strength, probably because of the influence of the coligands or the slightly different geometries of the Pt–CH= moieties. For example, for the two protons at 1-H and at 6-H (for HEX) or at 1-H and at 7-H (for All_2O), $^2J_{Pt,H(=CH)}$ is generally larger for the protons in the *E* position to protons 2-

Table 2. Selected chemical shifts [ppm] and coupling constants [Hz] of the diolefin Pt complexes.[a]

Complex	H	δ ^{1}H, $^2J_{Pt,H}$	H	δ ^{1}H, $^2J_{Pt,H}$	$^2J_{Pt,CH_3}$	δ ^{195}Pt[e]
[(COD)PtCl$_2$]	1,2-H	5.61, 67	5,6-H	5.61, 67	–	–3332
[(Me$_2$COD)PtCl$_2$]	1,2-H	5.42, 63	5,6-H	5.42, 63	–	–3252
[(NBD)PtCl$_2$]	2,3-H	5.30, 68	5,6-H	5.30, 68	–	–3118
[(HEX)PtCl$_2$]	2,5-H	5.71, 61	1,6-H (*E*)	5.10, 65	–	–3423
			1,6-H (*Z*)	4.51, 57		
[(All$_2$O)PtCl$_2$]	2,6-H	5.77, 61	1,7-H (*E*)	5.05, 65	–	
			1,7-H (*Z*)	4.53, 50		
[(COD)Pt(Me)$_2$][b]	1,2-H	4.77, 42	5,6-H	4.77, 42	83	–3572
[(Me$_2$COD)Pt(Me)$_2$]	2-H	4.58, 36	6-H	4.58, 36	82	–3479
[(NBD)Pt(Me)$_2$][b]	2,3-H	5.04, 40	5,6-H	5.04, 40	91	–3609
[(NBD)Pt(Bn)$_2$][b]	2,3-H	4.73, 41	5,6-H	4.73, 41	–	–3635
[(Me$_2$COD)Pt(C$_6$F$_5$)$_2$][b]	2-H	5.30, 42	6-H	5.30, 42	–	–3436
[(HEX)Pt(C$_6$F$_4$H-5)$_2$][b]	2,5-H	5.66, 50	1,6-H (*Z*)	4.82, 45	–	
			1,6-H (*E*)	4.65, 42		
[(HEX)Pt(C$_6$F$_4$H-4)$_2$]	2,5-H	5.60, –[d]	1,6-H (*Z*)	4.83, 45	–	
			1,6-H (*E*)	4.31, 41		
[(COD)Pt(Me)Cl][b]	1,2-H	5.42, 36	5,6-H	4.54, 75	73	–3501
[(Me$_2$COD)Pt(Me)Cl]	2-H	5.33, 41	6-H	4.27, 68	74	–3436
[(NBD)Pt(Me)Cl][b]	2,3-H	5.56, 32	5,6-H	4.89, 77	77	–3566
[(HEX)Pt(Me)Br][b]	2-H	5.35, 34	5-H	4.79, 64	72	–3764
	1-H (*E*)	5.52, 33	6-H (*E*)	3.54, 72		
	1-H (*Z*)	4.59, 46	6-H (*Z*)	3.73, 71		
[(NBD)Pt(Bn)Cl][b]	2,3-H	5.49, 33	5,6-H	4.23, 77	–	–3566
[(COD)Pt(Me)(C≡C(4-Me)Ph)][c]	1,2-H	5.64, 37	5,6-H	4.91, 50	79	–3209
[(COD)Pt(C≡C(4-Me)Ph)$_2$][c]	1,2-H	5.64, 45	5,6-H	5.64, 45	–	–3209
[(Me$_2$COD)Pt(Me)(C≡C(4-Me)Ph)]	2-H	5.35, 31	6-H	4.67, 45	76	–3693
[(Me$_2$COD)Pt(C≡C(4-Me)Ph)$_2$]	2-H	5.48, 39	6-H	5.48, 39	–	–3773
[(COD)Pt(Bn)$_2$][b]	2-H	4.68, 42	6-H	4.68, 42	–	–3646
[(COD)Pt(Bn)Cl][b]	2-H	5.48, 38	6-H	4.45, 75	–	–3507
[(COD)Pt(Bn)(MQ)][PF$_6$]$_2$[b]	2-H	5.52, 36	6-H	5.47, 72	–	–3670
[(COD)Pt(Me)(MQ)][PF$_6$]$_2$[b]	2-H	5.54, 30	6-H	5.35, 78	69	–3662
[(COD)Pt(Bn)(Mpz)][PF$_6$]$_2$[b]	2-H	5.58, 36	6-H	5.28, 85	–	–3618

[a] Measured in $CDCl_3$ unless indicated otherwise. For unsymmetrical complexes, the stronger coligand is located *trans* to 1,2(3)-H; *E* or *Z* correspond to the orientation of the H atom relative to 2,5(6)-H. For the numbering of the ligands, see Scheme 2. [b] Measured in [D$_6$]acetone. [c] Measured in CD_2Cl_2. [d] No clear satellites detectable owing to overlap with the main signal. [e] External standard for ^{195}Pt (I = 1/2, natural abundance 33.8%) chemical shift: $Na_2[PtCl_6]$ in D_2O.

H and 5-H (or 2-H and 6-H; for example, see the different values for the *Z*- and *E*-oriented protons of the HEX complexes in Table 2).

As repulsions between the methyl substituents of Me_2-COD and the coligands at the Pt atom might have an impact on the NMR spectroscopic data, we checked the molecular structures of the two Me_2COD complexes from XRD and performed NOE measurements. However, strong NOEs were not observed in the NMR spectra of [(Me_2-COD)Pt($Me)_2$] or [(Me_2COD)Pt($C_6F_5)_2$]. For the latter complex, this is in line with the shortest Me···F–C_6F_4 distance of 3.32(1) Å.

All of the "organic" coligands Me, Bn, C≡C(4-Me)Ph and C_6F_5 exert rather strong donor behaviour, and $^2J_{Pt,H(=CH)}$ of the *trans*-oriented olefin group ranges from 36 to 45 Hz. The resonances for the "unsymmetric" olefin ligands HEX and All_2O have been unequivocally assigned on the basis of 2D experiments, and the data reveals marked differences for the three or six individual signals.

Another important NMR parameter is the ^{195}Pt NMR chemical shift (Table 2), and the values for the new complexes are in the typical range for Pt^{II} complexes.[41e,50] Although no correlation can be drawn between the (electronic) structures of the complexes and the chemical shift values, the exceedingly broad scale of the ^{195}Pt NMR chemical shift usually allows the unequivocal detection of such complexes even in complex mixtures.[41e,49a,51]

Ligand Exchange Reactions of *cis*-[(‖^‖)$PtCl_2$] with Diisopropyl-1,4-diazabutadiene

To assess the assumed higher reactivity of the diolefin complexes compared with the COD derivatives, we performed ligand exchange reactions of ‖^‖ with diisopropyl-1,4-diazabutadiene (*i*Pr-DAB). To solutions of the diolefin complexes in CH_2Cl_2, we added 10 equiv. of the ligand *i*Pr-DAB dissolved in CH_2Cl_2. The reaction progress was measured by UV/Vis spectroscopy (for an example, see Figure 4). The appearance of a band at λ = 482 nm indicates the formation of [(*i*Pr-DAB)$PtCl_2$] and was used to calculate the reaction rates (Table 3).

While COD and Me_2COD exhibit qualitatively similar exchange rates, the other three diolefin complexes were far more labile (Table 3). This correlates quite well with the $^2J_{Pt,CH_3}$ coupling constants from the NMR spectroscopic data and suggests that Me_2COD and COD have approximately the same ligand strength, whereas NBD seems to be markedly weaker. In contrast, the $^2J_{Pt,H(=CH)}$ values for these chlorido complexes suggest that the Pt–‖^‖ bond strength decreases along the series NBD ≈ COD > Me_2-COD > HEX ≈ All_2O, which does not agree with the ligand exchange experiments at all. As diene ligands exert quite a strong *trans* effect but a modest *trans* influence,[49d] it is perhaps not surprising that bond strength indications from $^2J_{Pt,H(=CH)}$ values do not correlate with rates of loss of diene ligands. Kinetic factors have an impact on the reaction rates with COD and Me_2COD, which profit from the "double chelate" binding of their ring structure, compared with those with the open chain structures of HEX and All_2O. For NBD, we assume that the well-established steric strain of the unsaturated six-membered ring is the reason for the rapid decoordination.

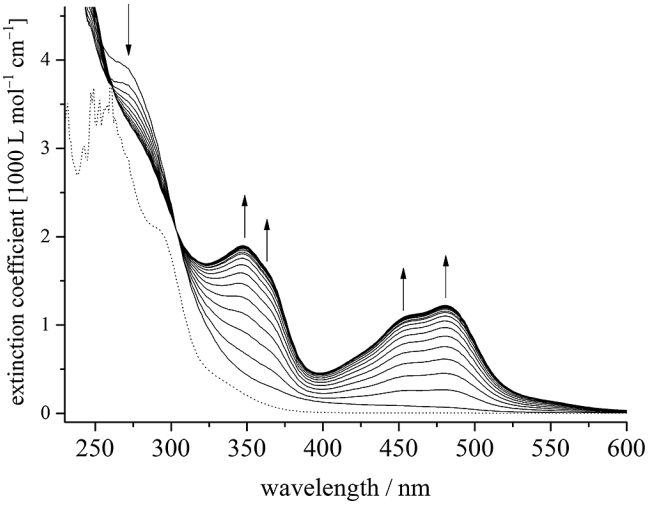


Figure 4. Time-dependent absorption spectra of the formation of [(*i*Pr-DAB)$PtCl_2$] from [(All_2O)$PtCl_2$] and *i*Pr-DAB in CH_2Cl_2 (the dotted line represents the starting complex).

Table 3. Rate constants *k* of the ligand exchange reactions of the olefin complexes with *i*Pr-DAB.[a]

Complex	Rate constant *k* [mol L^{-1} s^{-1}]
[(COD)$PtCl_2$]	2.37×10^{-7}
[(Me_2COD)$PtCl_2$]	2.83×10^{-7}
[(HEX)$PtCl_2$]	1.53×10^{-4}
[(NBD)$PtCl_2$]	6.21×10^{-4}
[(All_2O)$PtCl_2$]	8.08×10^{-4}
[(dmso)$_2PtCl_2$][b]	3.40×10^{-3}

[a] Reaction in CH_2Cl_2. [b] For comparison, *cis*-[(dmso)$_2PtCl_2$] was tested.

Cytotoxicity

In continuation of our previous work on the cytotoxicity of organoplatinum(II)–COD complexes, we extended our study to platinum complexes with various diolefin ligands and evaluated their antiproliferative properties in HT-29 colon carcinoma and MCF-7 breast adenocarcinoma cell lines in a comparative manner. Previous studies on platinum–COD species had indicated that the replacement of one chlorido coligand of [(COD)$PtCl_2$] with a methyl ligand resulted in a considerable increase in cytotoxic potency.[13a,13b] The introduction of different substituted phenylalkynyl coligands in the position of the chlorido coligand led to species with activities in the range of 0.2 to 30 μM. By replacing the methyl coligand with a second phenylalkynyl coligand, symmetric bis-alkynyl platinum complexes with an increased antiproliferative activity in the submicromolar range were obtained. The highest activity was observed for the *m*-methyl-substituted phenylalkynyl complex [(COD)-

Table 4. Cytotoxicity of selected diolefin Pt complexes.

	IC_{50} HT-29 [μM]	IC_{50} MCF-7 [μM]	Reference
cisplatin	7.0 ± 2.0	2.0 ± 0.3	[52]
[(COD)$PtCl_2$]	>100	>100	[13d]
[(COD)Pt(Me)Cl]	8.3 ± 3.0	11.2 ± 1.4	[13d]
[(COD)Pt$(Me)_2$]	>100	>100	this work
[(COD)Pt$(Ph)_2$]	5.2 ± 0.6	7.2 ± 0.7	this work
[(COD)Pt$(Bn)_2$]	13.4 ± 2.1	15.4 ± 3.4	this work
[(COD)Pt(Bn)Cl]	10.2 ± 3.5	9.8 ± 1.0	[13a]
[(COD)Pt(Bn)(C≡C(4-Me)Ph)]	1.3 ± 0.0	2.1 ± 0.9	[13a]
[(COD)Pt(Bn)(MQ)][PF_6]$_2$	12.2 ± 3.2	9.6 ± 0.6	this work
[(COD)Pt(Bn)(Mpz)][PF_6]$_2$	11.2 ± 2.9	7.2 ± 2.1	this work
[(COD)Pt$(C_6F_5)_2$]	>100	94.1 ± 2.0	this work
[(COD)Pt$(C≡C(4\text{-}Me)Ph)_2$]	0.4 ± 0.1	0.3 ± 0.0	[13a]
[$(Me_2COD)PtCl_2$]	>100	>100	this work
[(Me_2COD)Pt(Me)Cl]	20.0 ± 6.0	10.5 ± 2.0	this work
[(Me_2COD)Pt$(C_6F_5)_2$]	>100	15.0 ± 1.2	this work
[(Me_2COD)Pt$(C≡C(4\text{-}Me)Ph)_2$]	1.4 ± 1.2	4.0 ± 0.5	this work
[(HEX)$PtCl_2$]	53.2 ± 6.8	39.9 ± 8.6	this work
[(HEX)Pt$(C_6F_4H\text{-}4)_2$]	1.9 ± 0.4	1.2 ± 0.3	this work
[(HEX)Pt$(C_6F_4H\text{-}5)_2$]	1.3 ± 0.2	1.1 ± 0.0	this work

Pt$(C≡C(3\text{-}Me)Ph)_2$], which exhibits a 10-fold higher activity than the platinum anticancer lead compound cisplatin and is also more active than its methyl-substituted derivative [(COD)Pt(Me)(C≡C(3-Me)Ph)].[13a] In this previous study, we also observed decomposition reactions of these alkynylplatinum complexes that are probably related to their high toxicity. Therefore, in the present study we included complexes containing weakly coordinated ligands, which could potentially lead to desirable ligand exchange reactions. These were the diolefin ligands Me_2COD, NBD, HEX, All_2O and All_2NH (Scheme 2), and these ligands were compared with COD. Alternatively, the weak coligands *N*-methyl-4,4′-bipyridinium (MQ^+) and *N*-methyl-1,4-pyrazinium (Mpz^+) were introduced instead of the chlorido coligand (Table 4). For further comparison with previous reports on cytotoxic organoplatinum complexes with perfluoroaryl coligands, we included also the 1,5-hexadiene complexes [(HEX)$PtCl_2$], [(HEX)Pt$(C_6F_4H\text{-}5)_2$] and [(HEX)Pt$(C_6F_4H\text{-}4)_2$]. The last complex showed remarkable toxicity against L1210 and cisplatin-resistant L2110 cell lines.[32a]

[$(Me_2COD)PtCl_2$], [(HEX)$PtCl_2$] and [(COD)$PtCl_2$] are essentially nontoxic; this confirms previous results, which showed that an organometallic coligand is essential for the activity. Interestingly, although the dimethyl complex [(COD)Pt$(Me)_2$] and the two pentafluorophenyl complexes [(COD)Pt$(C_6F_5)_2$] and [(Me_2COD)Pt$(C_6F_5)_2$] are not toxic, the corresponding benzyl and phenyl complexes exhibit marked toxicity. We explain the observed nontoxicity with the rather high stability of the Me and C_6F_5 complexes towards reductive elimination reactions (Bn much faster than Me, C_6H_5 much faster than C_6F_5),[53] In contrast to our expectations, the introduction of Me_2COD does not generally lead to enhanced toxicity, as the dialkynyl complexes with C≡C(4-Me)Ph coligands demonstrate. Enhanced toxicity against MCF-7 compared with the COD derivative is only found for [(Me_2COD)Pt$(C_6F_5)_2$]. Furthermore, the introduction of the weak coligands MQ^+ and Mpz^+ does not lead to increased toxicity compared with that of the chlorido derivative. Very probably, the cleavage of these labile ligands in the cell culture medium leads to the chlorido complex or at least to the same species that evolves from the chloride derivative in a similar manner to the cleavage of ethane from [$PtCl(C_2H_4)$(chxn)]Cl (chxn = *R*,*R*- or *S*,*S*-1,2-diaminocyclohexane).[43] Remarkably high antiproliferative effects have been found for the perfluorophenyl complexes of 1,5-hexadiene, confirming previous results.[32a] This is interesting as neither the corresponding chlorido complex [(HEX)$PtCl_2$] nor the COD or Me_2COD complexes containing the C_6F_5 coligand exhibit remarkable toxicity. Here, the higher lability of the diolefin ligand HEX leads to increased toxicity, which confirms the abovementioned study on platinum complexes with perfluoroaryl coligands. In this study, the toxicity of complexes containing two C_6F_4H-4 coligands increased within the series dmso < ethylenediamine < HEX < NBD.[32a] Marked differences in activity were also observed for different coligands, for example, the increasing activity for the HEX complexes within the series $C_6F_5 \approx C_6F_4H\text{-}2 < C_6F_4H\text{-}4 \approx C_6F_3H_2\text{-}3,5$ also points to a coligand-specific activity, probably a decomposition. Interestingly, no marked activity differences were observed in this study for individual compounds towards L1210 and cisplatin-resistant derivatives; this indicates a non-cisplatin-like mode of action, and most of the tested complexes in this series exhibited lower antiproliferative activity than the standard cisplatin.[32a] In our tests, we found many compounds with markedly higher activity than that of cisplatin.

In terms of structure–activity relationships (SAR), we can draw the following conclusions from these new experiments. The dialkynyl complexes [(COD)Pt$(C≡C(R')Ph)_2$] remain the most-toxic derivatives in this class of compounds, probably because of (so far not defined) favourable ligand exchange reactions with molecular targets. When the diolefin chelate ligands are changed towards weakly binding derivatives, these complexes become more labile towards de-

composition, but they probably do not reach the crucial molecular targets in the cell. Platinum complexes containing perfluoroaryl coligands remain interesting candidates. For the complexes [(HEX)Pt(C_6F_4H-4)$_2$] and [(HEX)Pt-(C_6F_4H-5)$_2$] presented here, a good match between the rather weak olefin ligand binding and the strong binding of the perfluoroaryl coligands seems to enhance the toxicity. Here, favourable decomposition reactions might also be the origin of the antiproliferative effect; however, far more detailed studies are required to elucidate such mechanisms.

Conclusions

In search of new potent cytotoxic organoplatinum complexes, we have synthesised and investigated a series of platinum(II) diolefin complexes *cis*-[(‖^‖)$PtCl_2$], *cis*-[(‖^‖)-PtCl(R)] and *cis*-[(‖^‖)Pt(R)$_2$] (R = Me, Bn or C_6F_5) with the chelate diolefin ligands (‖^‖) 1,5-cyclooctadiene (COD), 1,5-dimethylocta-1,5-diene (Me_2COD), norbornadiene (NBD), 1,5-hexadiene (HEX), 3-allyloxypropene (All_2O, diallyl ether) and diallylamine (All_2NH). Although the reaction sequence [(‖^‖)$PtCl_2$]→[(‖^‖)Pt-(R)$_2$]→[(‖^‖)Pt(R)Cl] worked well for COD, Me_2COD and NBD, the complex [(HEX)Pt(Me)Cl] was obtained directly from [(HEX)$PtCl_2$] and MeMgBr. The corresponding reactions for the All_2O or All_2NH derivatives failed. The reactions of [(‖^‖)$PtCl_2$] and [(‖^‖)Pt(R)Cl] with HC≡C(4-Me)-Ph in the presence of a base gave [(‖^‖)Pt(C≡C(4-Me)-Ph)] or [(‖^‖)Pt(R)(C≡C(4-Me)Ph)$_2$] only for the COD and Me_2COD derivatives; the other reactions generally failed. For some reactions with MeMgBr, the well-known tetrameric Pt^{IV} compound [$(PtMe_3)_4\mu_3$-Br_4] was obtained, and black unidentifiable material was also obtained in most reactions. The relative exchange rates of *cis*-[(‖^‖)$PtCl_2$] complexes towards the diimine ligand diisopropyl-1,4-diazabutadiene (*i*Pr-DAB) increased along the series COD < Me_2COD < NBD < HEX < All_2O by a factor of 4. Clearly, the ease of the olefin ligand exchange coincides with the difficulty of the transmetallation reactions to obtain alkyl or alkynyl derivatives. For the latter ligands, we assume that the nucleophilic attack of the alkyl or alkynyl carbanion to the olefin moiety dominates over the transmetallation but does not yield stable products. The complex [(All_2NH)-$PtCl_2$]$_2$ undergoes a unique rearrangement process in DMSO solution to yield the dimeric piperazine complex [PtCl(dmso)($C_6H_{10}N$)]$_2$, which has been characterised by single-crystal XRD and contains the remarkable bridging (1,4-diallylpiperazine-2,5-diyl)dimethanide(2$^-$) ligand. Selected platinum complexes were submitted to cytotoxicity experiments with HT-29 colon carcinoma and MCF-7 breast cancer cell lines. For comparison, the dicationic complexes [(COD)Pt(Bn)(L)][PF_6]$_2$ with the very labile coligands *N*-methyl-4,4′-bipyridinium (MQ^+) and *N*-methyl-1,4-pyrazinium (Mpz^+) were added. The study clearly shows that neither labile diolefin ligands nor the labile MQ^+ or Mpz^+ coligands lead to markedly increased cytotoxicity for the established alkyl/chlorido, alkyl/alkynyl or dialkynyl platinum complex systems. However, the introduction of the weakly binding 1,5-hexadiene ligand yielded the rather toxic complexes [(HEX)Pt(C_6F_4H-4)$_2$] and [(HEX)Pt-(C_6F_4H-5)$_2$] with perfluoroaryl coligands. A comparison with a previous study on such perfluoroaryl platinum complexes substantiates our initial assumption that the organometallic complexes under study exhibit some favourable decomposition reactions in the cell that lead to apoptosis (by a not yet understood mechanism). The most-toxic compounds seem to combine a high occurrence of this favourable reaction (presumably reductive elimination) with a relatively high general complex stability, which allows them to reach crucial spots in the cell.

Experimental Section

Instrumentation: The NMR spectra were recorded with a Bruker Avance II 300 MHz spectrometer (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz, ^{19}F: 282.23 MHz), a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{195}Pt: 86.01 MHz) with a triple resonance ^{1}H,^{19}F,BB inverse probehead, a Bruker Avance II 600 spectrometer (^{1}H: 600.13 MHz) or a Bruker DPX 300 spectrometer (^{19}F: 282.23 MHz). The broadband coil was tuned to either the carbon or the platinum frequency, and the detection coil was tuned to the proton frequency, which resulted in 90° pulses of 11.9 μs for ^{13}C, 12.5 μs for ^{195}Pt and 12.4 μs for ^{1}H. The unambiguous assignment of the ^{1}H, ^{13}C and ^{195}Pt resonances was obtained from ^{1}H TOCSY, ^{1}H COSY, ^{1}H NOESY, gradient-selected ^{1}H, ^{13}C heteronuclear single quantum coherence (HSQC) and HMBC, and gradient-selected ^{1}H–^{195}Pt HMBC experiments. All 2D NMR experiments were performed with standard pulse sequences from the Bruker pulse program library. Chemical shifts are reported relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C, $CFCl_3$ for ^{19}F and $Na_2[PtCl_6]$ in D_2O for ^{195}Pt. The spectra were analysed with the Bruker TopSpin 2 software. ESI-MS spectra were recorded with a Finnigan MAT 900 S instrument, and EI-MS spectra were recorded with a Finnigan MAT 95 instrument. Simulations were done with ISOPRO 3.0. Elemental analyses were performed with a Hekatech CHNS EuroEA 3000 analyser. IR spectra were recorded with a Bruker IFS 66v/s spectrometer.

Single-Crystal X-ray Analysis: Data collection was performed with a STOE IPDS I diffractometer with Mo-K_α radiation (λ = 0.71073 Å) by employing the ω–2θ scan technique at T = 293(2) K for all four compounds and additionally at 100(2) K for [(Me_2COD)$PtCl_2$]. The structures were solved by direct methods by using the SHELXTL package,[54] and refinement was performed with SHELXL97 by employing full-matrix least-squares methods on F^2[55] with $F_o^2 \geq 2\sigma(F_o^2)$; the results are shown in Table 1 (and the Supporting Information). All non-hydrogen atoms were treated anisotropically, and hydrogen atoms were included by using appropriate riding models. The structure of [(Me_2COD)$PtCl_2$] was solved for the datasets at both 293 and 100 K in the orthorhombic space group *Ccmm* with rather good *R* values. However, the high symmetry falsely leads to the identity of all four olefinic =C atoms and all four –CH_2– groups. Attempts to lower the symmetry for a structure solution failed.

CCDC-1006480 {for [(Me_2COD)$PtCl_2$]}, -1006481 {for [(Me_2-COD)Pt(C_6F_5)$_2$]}, -1006482 {for [(dmso)PtCl($C_6H_{10}N$)]$_2$} and -10066483 {for [(HEX)$PtCl_2$]} contain the full crystallographic data. These data can be obtained free of charge from The Cam-

bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cytotoxicity Experiments: The antiproliferative effects of the compounds were determined by following an established procedure.[56] Briefly, the cells were suspended in cell culture medium (HT-29: 2850 cells/mL, MCF-7: 10000 cells/mL), and 100 μL aliquots were plated in 96-well plates and incubated at 37 °C with 5% CO_2 for 48 (HT-29) or 72 h (MCF-7). Stock solutions of the compounds in dimethylformamide (DMF) were freshly prepared and diluted with cell culture medium to the desired concentrations (final DMF concentration: 0.1% v/v). The medium in the plates was replaced with medium containing the compounds in graded concentrations (six replicates). After further incubation for 72 (HT-29) or 96 h (MCF-7), the cell biomass was determined by crystal violet staining, and the IC_{50} values were determined as those concentrations that caused 50% inhibition of cell proliferation. The results were calculated from two independent experiments.

Materials and Procedures: All preparations were performed in a dry argon atmosphere by using Schlenk techniques. Solvents (CH_2Cl_2, THF, toluene, diethyl ether and MeCN) were dried with an MBRAUN MB SPS-800 solvent purification system. The complexes [(COD)$PtCl_2$],[57] [(COD)$Pt(Me)_2$],[11a,13b,57] [(COD)Pt(Me)Cl],[11a,13b,57] [(COD)$Pt(Bn)_2$],[13b] [(COD)Pt(Bn)Cl],[13b] [(COD)$Pt(C{\equiv}C(4\text{-}Me)Ph)_2$],[13a] [(COD)Pt(Me)(C≡C(4-Me)Ph)],[13a] [(COD)Pt(Bn)(C≡C(4-Me)Ph)],[13a] [(COD)$Pt(Ph)_2$],[11b,14b] [(COD)$Pt(C_6F_5)_2$],[32c] [(NBD)$PtCl_2$],[29] [(HEX)$PtCl_2$][58] and [$(dmso)_2PtCl_2$][59] were prepared according to published procedures. The complexes [(Me_2COD)$PtCl_2$], [(All_2O)$PtCl_2$] and [(All_2NH)$PtCl_2$] have been synthesised in a similar procedure to that described by Clark and Manzer for [(COD)$PtCl_2$];[57] alternative methods have been described elsewhere.[38,60,61] All other chemicals were purchased from commercial suppliers and were used without further purification. The complex [(HEX)$Pt(C_6F_4H\text{-}4)_2$] was prepared as described previously.[32c]

Synthesis of [(Me_2COD)$PtCl_2$] [(NBD)$PtCl_2$], [(HEX)$PtCl_2$], [(All_2O)$PtCl_2$] and [(All_2NH)$PtCl_2$]: In a prototypical reaction for [(Me_2COD)$PtCl_2$], $K_2[PtCl_4]$ (500 mg, 1.2 mmol) was dissolved in water/2-propanol (50:50 vol.-%, 60 mL). To the red solution, an excess of 1,5-dimethylcycloocta-1,5-diene (7 equiv.) was added and stirred at 70 °C overnight. The colourless solid that formed was collected by filtration, washed with water, ethanol and diethyl ether, and dried under reduced pressure. The product was purified by recrystallisation from CH_2Cl_2/*n*-heptane.

[(Me_2COD)$PtCl_2$]: Yield 352 mg (0.876 mmol, 73%). $C_{10}H_{16}Cl_2Pt$ (402.23): calcd. C 29.86, H 4.01; found C 29.78, H 3.98. ^{1}H NMR ($CDCl_3$): δ = 5.42 (m, $^2J_{Pt,H}$ = 63 Hz, 2 H, =CH), 2.84–2.71 (m, 2 H, CH_2), 2.46–2.28 (m, 4 H, CH_2), 2.14–2.03 (m, 2 H, CH_2), 1.92 (s, $^3J_{Pt,H}$ = 41 Hz, 6 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3252 ppm.

[(NBD)$PtCl_2$]: Yield 378 mg (1.056 mmol, 88%). $C_7H_8Cl_2Pt$ (358.13): calcd. C 23.48, H 2.25; found C 23.51, H 2.23. ^{1}H NMR ([D$_6$]acetone): δ = 5.34 (m, $^2J_{Pt,H}$ = 69 Hz, 4 H, =CH), 4.42 (m, $^3J_{Pt,H}$ = 18 Hz, 2 H, 1-H, 4-H), 1.76 (m, $^4J_{Pt,H}$ = 3 Hz, 2 H, 7-H) ppm. ^{195}Pt,^{1}H HMBC ([D$_6$]acetone): δ = –3720 ppm.

[(HEX)$PtCl_2$]: Yield 343 mg (0.985 mmol, 82%). $C_6H_{10}Cl_2Pt$ (348.13): calcd. C 20.70, H 2.90; found C 20.59, H 2.88. ^{1}H NMR ([D$_6$]acetone): δ = 5.68 (m, $^2J_{Pt,H}$ = 60 Hz, 2 H, =CH), 4.94 [d, $^2J_{Pt,H}$ = 65 Hz, $^3J_{H,H}$ = 8 Hz, 2 H, =CH_2 (*E*)], 4.52 [d, $^2J_{Pt,H}$ = 58 Hz, $^3J_{H,H}$ = 13 Hz, 2 H, =CH_2 (*Z*)], 2.87–2.67 (m, 2 H, CH_2), 2.63–2.34 (m, 2 H, CH_2) ppm. ^{195}Pt,^{1}H HMBC ([D$_6$]acetone): δ = –3431 ppm.

[(All_2O)$PtCl_2$]: Yield 406 mg (1.115 mmol, 93%). $C_6H_{10}Cl_2OPt$ (364.13): calcd. C 19.79, H 2.77; found C 19.69, H 2.80. ^{1}H NMR ($CDCl_3$): δ = 5.77 (m, $^2J_{Pt,H}$ = 61 Hz, 2 H, =CH), 5.05 [d, $^2J_{Pt,H}$ = 65 Hz, 2 H, =CH_2 (*E*)], 4.53 [d, $^2J_{Pt,H}$ = 50 Hz, 2 H, =CH_2 (*Z*)], 4.02–3.74 (m, 4 H, CH_2) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3618 ppm.

When the same procedure was used to synthesise [(All_2NH)$PtCl_2$], an insoluble yellow powder was obtained. This powder is presumably the dimeric complex [(All_2NH)$PtCl_2$]$_2$ (see text), yield 318 mg (0.876 mmol, 73%). $C_{12}H_{22}Cl_4N_2Pt_2$ (726.28): calcd. C 19.84, H 3.05, N 3.86; found C 19.89, H 3.03, N 3.83. No NMR or MS spectra could be obtained owing to the virtual insolubility of the powder. IR (ATR): $\tilde{\nu}$ = 3193 (w), 3073 (w), 2935 (w), 2152 (w), 2043 (w), 1983 (w), 1616 (s), 1447 (s), 995 (s), 929 (s) cm^{-1}.

[(dmso)Pt$Cl(C_6H_{10}N)]_2$: $K_2[PtCl_4]$ (500 mg, 1.2 mmol) was dissolved in water/2-propanol (50:50 vol.-%, 60 mL). To the red solution, All_2NH (580 mg, 8.4 mmol, 7 equiv.) was added, and the mixture was stirred at 25 °C overnight. The yellow solid [(All_2NH)$PtCl_2$]$_2$ formed in this first reaction was collected by filtration, washed with water, ethanol and diethyl ether, and dried under reduced pressure. The complete amount of [(All_2NH)$PtCl_2$]$_2$ was heated in DMSO until it dissolved, and crystallisation by slow evaporation over 3 d yielded colourless crystals (62 mg, 0.08 mmol, 6%). $C_{16}H_{32}Cl_2N_2O_2Pt_2S_2$ (809.64): calcd. C 23.74, H 3.98, N 3.46; found C 23.79, H 3.93, N 3.41. No NMR or MS spectra could be obtained owing to the virtual insolubility of the product. The residual yellow material (610 mg, 0.84 mmol, 70%) was the dimeric complex [(All_2NH)$PtCl_2$]$_2$ (vide supra).

[(NBD)$Pt(Me)_2$]: [(NBD)$PtCl_2$] (1.4 g, 3.91 mmol) was suspended in diethyl ether (20 mL) and stirred at –50 °C. To this mixture was added slowly methylmagnesium bromide (3 M solution in THF, 4.3 mL, 12.9 mmol, 2.2 equiv.) and diethyl ether (40 mL). The reaction mixture was stirred for another 15 min at –50 °C and warmed over 3 h to ambient temperature while stirring. The solution was hydrolysed at –10 °C by the dropwise addition of water (18 mL). After the mixture warmed to ambient temperature, conc. HCl (1 mL) was added, and the layers were separated. The aqueous layer was extracted three times with CH_2Cl_2 (20 mL), the combined organic layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The colourless product [(NBD)$Pt(Me)_2$] was purified by recrystallisation from CH_2Cl_2/*n*-heptane, yield 1015 mg (3.2 mmol, 82%). $C_9H_{14}Pt$ (317.29): calcd. C 34.07, H 4.45; found C 33.98, H 4.38. ^{1}H NMR ([D$_6$]acetone): δ = 5.04 (m, $^2J_{Pt,H}$ = 40 Hz, 4 H, =CH), 4.04 (m, 2 H, CH), 1.57 (m, 2 H, CH_2), 0.60 (s, $^2J_{Pt,H}$ = 91 Hz, 6 H, CH_3) ppm. EI-MS: *m*/*z* = 317 [M]$^+$.

[(NBD)Pt(Me)Cl]: [(NBD)$Pt(Me)_2$] (1 g, 3.15 mmol) was dissolved in acetone (50 mL) and methanol (2 mL) and cooled to –55 °C, and an acetyl chloride (336 μL, 4.725 mmol, 1.5 equiv.) solution was added. After the reaction mixture was stirred for 1.5 h at room temperature, the solvent was removed under reduced pressure, and the product was washed five times with pentane, yield 987 mg (2.92 mmol, 93%). $C_8H_{11}ClPt$ (337.71): calcd. C 28.45, H 3.28; found C 28.53, H 3.30. ^{1}H NMR ([D$_6$]acetone): δ = 5.56 (m, $^2J_{Pt,H}$ = 32 Hz, 2 H, =$CH_{2,3}$), 4.89 (m, $^2J_{Pt,H}$ = 77 Hz, 2 H, =$CH_{5,6}$), 4.15 (m, 2 H, CH), 1.81 (m, 2 H, CH_2), 0.67 (s, $^2J_{Pt,H}$ = 86 Hz, 3 H, CH_3) ppm. EI-MS: *m*/*z* = 337 [M$^+$].

[(NBD)$Pt(Bn)_2$]: [(NBD)$PtCl_2$] (1.0 g, 2.793 mmol) was suspended in diethyl ether (25 mL) and stirred at –54 °C. To this mixture, the Grignard solution prepared from Mg turnings (650 mg, 26.7 mmol) and benzyl chloride (3.38 g, 26.7 mmol) in diethyl ether (60 mL) was added slowly. The reaction mixture was stirred for another

15 min at –54 °C and warmed over 2 h to ambient temperature while stirring. After the addition of diethyl ether (50 mL), the solution was cooled to –20 °C and hydrolysed by the dropwise addition of water (20 mL). After warming to ambient temperature, conc. HCl (2 mL) and water (50 mL) were added, and the layers were separated. The aqueous layer was extracted three times with CH_2Cl_2 (20 mL), the combined organic layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The resulting yellow oil was purified by recrystallisation from CH_2Cl_2/*n*-heptane to yield colourless [(NBD)Pt(Bn)$_2$] (1035 mg, 2.2 mmol, 79%). $C_{21}H_{22}Pt$ (469.48): calcd. C 53.72, H 4.72; found C 53.98, H 4.68. ^{1}H NMR ([D$_6$]acetone): δ = 7.42–6.96 (m, 10 H, ArH), 4.37 (m, $^2J_{Pt,H}$ = 41 Hz, 4 H, =CH), 3.74 (m, 2 H, CH), 2.93 ($^2J_{Pt,H}$ = 118 Hz, s 4 H, CH_2Ph), 1.39 (m, 2 H, NBD CH_2) ppm. ^{195}Pt,^{1}H HMBC ([D$_6$]acetone): δ = –3635 ppm. EI-MS: *m*/*z* = 469 [M]$^+$.

[(NBD)Pt(Bn)Cl]: [(NBD)Pt(Bn)$_2$] (1 g, 2.13 mmol) was dissolved in acetone (50 mL) and methanol (2 mL) at –55 °C, and a solution of acetyl chloride (228 μL, 3.2 mmol, 1.5 equiv.) was added. After the reaction mixture was stirred for 2 h at ambient temperature, the solvent was removed under reduced pressure, and the product was washed five times with pentane, yield 820 mg (1.98 mmol, 93%). $C_{14}H_{15}ClPt$ (413.81): calcd. C 40.63, H 3.65; found C 40.53, H 3.60. ^{1}H NMR ([D$_6$]acetone): δ = 7.40–6.96 (m, 5 H, ArH), 5.49 [m, $^2J_{Pt,H}$ = 33 Hz, 2 H, =CH$_{(2,3)}$], 4.23 [m, $^2J_{Pt,H}$ = 77 Hz, 2 H, =CH$_{(5,6)}$], 4.02 (m, 2 H, CH), 2.99 (s, $^2J_{Pt,H}$ = 120 Hz, 2 H, CH_2Ph), 1.76–1.62 (m, 2 H, NBD CH_2) ppm. ^{195}Pt,^{1}H HMBC ([D$_6$]acetone): δ = –3432 ppm. EI-MS: *m*/*z* = 413 [M]$^+$.

[(HEX)Pt(C_6F_4H-5)$_2$]: [(HEX)PtCl$_2$] (1.39 g, 4.00 mmol) and 2,3,4,6-tetrafluorophenyllithium[62] (from 1-bromo-2,3,4,6-tetrafluorobenzene, 1.83 g, 8.00 mmol) and *n*BuLi (5.00 mL, 8.00 mmol) were stirred together in diethyl ether (40 mL) under nitrogen at –78 °C for 2 h. The reaction mixture was slowly warmed over 0.5 h to –25 °C and it was then hydrolysed with aqueous NH_4Cl (5% w/v). Ether extraction and evaporation provided a mixture of two compounds (TLC). Treatment with minimum diethyl ether yielded a white solid and a yellow oil (which was discarded). The white powder was washed with hexane and dried (not recrystallised), yield 1.43 g, 62%; m.p. 175–180 °C (dec.). $C_{18}H_{12}F_8Pt$ (575.36): calcd. C 37.60, H 2.10; found C 37.53, H 2.14. ^{19}F NMR ([D$_6$]-acetone): δ = –93.9 (m, $^3J_{Pt,F}$ = 332 Hz, 1 F, 6-F), –94.7 (m, $^3J_{Pt,F}$ = 325 Hz, 1 F, 6-F), –113.5 (m, $^3J_{Pt,F}$ = 373 Hz, 1 F, 2-F), –114.2 (m, $^3J_{Pt,F}$ = 363 Hz, 1 F, 2-F), –140.9 (m, 2 F, 4-F), –168.2 (m, 2 F, 3-F) ppm. ^{1}H NMR ([D$_6$]acetone): δ = 6.71 (m, 2 H, 5-H, 5′-H), 5.66 (m, $^2J_{Pt,H}$ = 50 Hz, 2 H, HEX 2-H, 5-H), 4.82 [d, $^3J_{H,H}$ = 8 Hz, $^2J_{Pt,H}$ = 45 Hz, 2 H, =CH (*Z*)], 4.65 [d, $^3J_{H,H}$ = 16 Hz, $^2J_{Pt,H}$ = 42 Hz, 2 H, =CH (*E*)], 2.77 (m, 2 H, CH_2), 2.55 (m, 2 H, CH_2) ppm. IR (Nujol/hexachlorobutadiene): $\tilde{\nu}$ = 2954 (w), 1622 (vs), 1489 (vs), 1418 (vs), 1346 (m), 1338 (m), 1310 (w), 1277 (m), 1215 (m), 1138 (s), 1046 (vs), 1020 (vs), 832 (vs) cm^{-1}. ESI-MS (–): *m*/*z* (%) = 574 (98) [M – H]$^-$, 494 (100) [Pt($C_6F_4H)_2$ + H]$^-$.

Reaction of [(HEX)PtCl$_2$] with MeMgBr {Attempted Synthesis of [(HEX)Pt(Me)$_2$] or [(HEX)Pt(Me)Cl]}: Analogously to the synthesis of [(NBD)Pt(Me)$_2$] described above, [(HEX)PtCl$_2$] (1360 mg, 3.91 mmol) was treated with MeMgBr (3 M, solution in diethyl ether). After aqueous workup and phase separation, *n*-heptane (40 mL) was added to the organic phase, and the volume was reduced to 40 mL (by removal of the CH_2Cl_2 and diethyl ether), whereupon a brownish precipitate and colourless crystals were obtained. The evaporation of the heptane phase gave a small amount of yellow microcrystalline material. The colourless crystals and most of the brownish material was [($PtMe_3)_4\mu^3$-Br$_4$], yield (determined by ^{1}H NMR integration) ca. 776 mg (0.61 mmol, 62%). $C_{12}H_{36}Br_4Pt_4$ (1280.37): calcd. C 11.26, H 2.83; found C 11.29, H 2.88. ^{1}H NMR ($CDCl_3$): δ = 1.51 (s, $^2J_{Pt,H}$ = 79.2 Hz) ppm (compare ref.[46a]). Single crystals were submitted to XRD experiments, but the resulting crystal structure was identical to that reported previously.[46b]

Parts of the brownish material and the small amount of yellow material were analysed as [(HEX)Pt(Me)Br], yield (determined by ^{1}H NMR integration) ≈ 320 mg (0.86 mmol, 22%). $C_7H_{13}BrPt$ (372.17): calcd. C 22.59, H 3.52; found C 22.63, H 3.62. ^{1}H NMR ([D$_6$]acetone): δ = 5.52 [m, $^2J_{Pt,H}$ = 33 Hz, $^3J_{H,H}$ = 8.5 Hz, 1 H, 1-H (*E*)], 5.35 (m, $^2J_{Pt,H}$ = 34 Hz, $^3J_{H,H}$ = 16 Hz, $^3J_{H,H}$ = 8.5 Hz, 1 H, 2-H), 4.79 (m, $^2J_{Pt,H}$ = 64 Hz, $^3J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, 5-H), 4.59 [m, $^2J_{Pt,H}$ = 46 Hz, $^3J_{H,H}$ = 16 Hz, 1 H, 1-H (*Z*)], 3.73 [m, $^2J_{Pt,H}$ = 71 Hz, $^3J_{H,H}$ = 13.6 Hz, 1 H, 6-H (*Z*)], 3.54 [m, $^2J_{Pt,H}$ = 72 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, 6-H (*E*)], 2.97–2.16 (m, 4 H, CH_2), 0.95 (s, $^2J_{Pt,H}$ = 72 Hz, 3 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ([D$_6$]acetone): δ = –3764 ppm. EI-MS: *m*/*z* = 372 [M]$^+$.

[(Me$_2$COD)Pt(Me)$_2$]: [(Me$_2$COD)PtCl$_2$] (76 mg, 0.188 mmol) was suspended in diethyl ether (10 mL) and stirred at –5 °C. To this mixture was added slowly methylmagnesium bromide (3 M solution in tetrahydrofuran, 140 μL, 0.414 mmol, 2.2 equiv.), and the reaction mixture was stirred for 1 h at –5 °C and for 3 h at room temperature. The solution was hydrolysed with water (15 mL), and the layers were separated. The aqueous layer was extracted three times with CH_2Cl_2 (20 mL), the combined organic layers were dried with magnesium sulfate, and the solvent was removed under reduced pressure. The yellow product was purified by recrystallisation from CH_2Cl_2/*n*-heptane, yield 66 mg (0.182 mmol, 97%). $C_{12}H_{22}Pt$ (361.40): calcd. C 39.88, H 6.14; found C 39.98, H 6.18. ^{1}H NMR ($CDCl_3$): δ = 4.58 (m, $^2J_{Pt,H}$ = 36 Hz, 2 H, =CH), 2.38–2.04 (m, 8 H, CH_2), 1.74 (s, $^3J_{Pt,H}$ = 26 Hz, 6 H, CCH_3), 0.68 (s, $^2J_{Pt,H}$ = 82 Hz, 6 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3479 ppm. EI-MS: *m*/*z* = 361 [M]$^+$.

[(Me$_2$COD)Pt(Me)Cl]: [(Me$_2$COD)Pt(Me)$_2$] (57 mg, 0.158 mmol) was dissolved in toluene (7 mL) and methanol (0.5 mL), cooled to 0 °C, and a solution of acetyl chloride (19 μL, 0.237 mmol, 1.5 equiv.) was added. After the reaction mixture was stirred for 1.5 h at room temperature, the solvent was removed under reduced pressure, and the product was washed five times with pentane, yield 48 mg (0.125 mmol, 79%). $C_{11}H_{19}ClPt$ (381.81): calcd. C 34.60, H 5.02; found C 34.55, H 5.01. ^{1}H NMR ($CDCl_3$): δ = 5.33 (m, $^2J_{Pt,H}$ = 41 Hz, 1 H, 2-H), 4.27 (m, $^2J_{Pt,H}$ = 68 Hz, 1 H, 6-H), 2.29–2.06 (m, 8 H, CH_2), 2.00 (s, $^3J_{Pt,H}$ = 11 Hz, 3 H, C-1–CH_3), 1.60 (s, $^3J_{Pt,H}$ = 67 Hz, 3 H, C-5–CH_3), 0.88 (s, $^2J_{Pt,H}$ = 74 Hz, 3 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3436 ppm. EI-MS: *m*/*z* = 381 [M]$^+$.

[(Me$_2$COD)Pt(C_6F_5)$_2$]: BrC_6F_5 (155 μL, 1.24 mmol) was dissolved in diethyl ether and stirred at –78 °C. *n*-Butyllithium (2.5 M solution in hexane, 510 μL) was added, and the mixture was stirred for 30 min. The mixture was then slowly added to a suspension of [(Me$_2$COD)PtCl$_2$] (250 mg, 0.67 mmol) in diethyl ether (20 mL). After 30 min, the reaction mixture was hydrolysed by the addition of diethyl ether/water (83/17 vol.-%). The layers were separated, and the organic layer was washed three times with water (10 mL). The solvent was removed under reduced pressure, and the product was purified by column chromatography (CH_2Cl_2/cyclohexane, 1:1, R_f = 0.6), yield 320 mg (72%). $C_{22}H_{16}F_{10}Pt$ (665.43): calcd. C 39.71, H 2.42; found C 39.75, H 2.41. ^{1}H NMR ([D$_6$]acetone): δ = 5.30 (m, $^2J_{Pt,H}$ = 42 Hz, 2 H, =CH), 2.77–2.53 (m, 8 H, CH_2), 1.80 (m, $^3J_{Pt,H}$ = 30 Hz, 6 H, CH_3) ppm. ^{19}F NMR ([D$_6$]acetone): δ = –120.0 (dd, 4 F), –162.8 (m, 2 F) –164.9 (m, 4 F) ppm. ^{195}Pt,^{1}H

HMBC ($CDCl_3$): δ = –3436 ppm. EI-MS: *m*/*z* = 330 [M – $2C_6F_5$]$^+$.

[(Me_2COD)Pt(C≡C(4-Me)Ph)$_2$]: The compound was prepared by a variation to the method described for [(COD)Pt(C≡CPh)$_2$]:[63] A suspension of [(Me_2COD)PtCl_2] (80 mg, 0.145 mmol) in ethanol (10 mL) was maintained at –5 °C, and a freshly prepared mixture of *p*-tolylacetylene (55 µL, 0.350 mmol, 2.2 equiv.) and *t*-BuOK (34 mg, 0.350 mmol, 2.2 equiv.) in ethanol (5 mL) was added dropwise with constant stirring. The solution became orange, and the solvent was removed under reduced pressure after 1 h. Recrystallisation from CH_2Cl_2/*n*-heptane gave the pure product as a microcrystalline yellow material, yield 62 mg (0.11 mmol, 76%). $C_{28}H_{30}Pt$ (561.20): calcd. C 59.88, H 5.38; found C 59.78, H 5.48. ^{1}H NMR ($CDCl_3$): δ = 7.29 (d, 4 H, *o*-Ph), 7.02 (m, 4 H, *m*-Ph), 5.48 (m, $^2J_{Pt,H}$ = 39 Hz, 2 H, =CH), 2.81–2.42 (m, 8 H, CH_2), 2.30 (s, 6 H, *p*-CH_3), 2.24 (s, $^3J_{Pt,H}$ = 32 Hz, 6 H, Me_2COD CH_3) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3773 ppm. IR (KBr): $\tilde{\nu}$ = 3072, 3043, 3025, 2996 [w, ν(C=C–H), 2911, 2888 [s, ν(HC–H) and ν(H_2C–H), 2117 [s, ν(C≡C)], 1604 (m), 1503 [s, ν(C=C) aryl], 1432, 1416 [m, δ(HC–H), δ(H_2C–H), 1005, 944, 924 (m), 843, 816, (s), 756, 712 [m, δ(C=C–H)] cm^{-1}. EI-MS: *m*/*z* = 561 [M]$^+$.

[(Me_2COD)Pt(Me)(C≡C(4-Me)Ph)]: The compound was prepared by a variation to the method described for [(COD)Pt(C≡CPh)$_2$]:[63] A suspension of [(Me_2COD)Pt(Me)Cl] (100 mg, 0.262 mmol) in ethanol (10 mL) was maintained at –5 °C, and a freshly prepared mixture of *p*-tolylacetylene (35 µL, 0.288 mmol, 1.1 equiv.) and potassium *tert*-butoxide (32 mg, 0.288 mmol, 1.1 equiv.) in ethanol (5 mL) was added dropwise with constant stirring. The solution became darker, and the reaction mixture was evaporated to dryness under reduced pressure after 1 h. Recrystallisation from CH_2Cl_2/*n*-heptane of the resulting solid gave the pure yellow microcrystalline product, yield 80 mg (0.173 mmol, 66%). $C_{20}H_{26}Pt$ (461.52): calcd. C 52.05, H 5.68; found C 52.04, H 5.71. ^{1}H NMR ($CDCl_3$): δ = 7.29 (d, 2 H, *o*-Ph), 7.02 (d, 2 H, *m*-Ph), 5.35 (m, $^2J_{Pt,H}$ = 31 Hz, 1 H, 2-H), 4.67 (m, $^2J_{Pt,H}$ = 45 Hz, 1 H, 6-H), 2.67–2.23 (m, 11 H, CH_2 and *p*-CH_3), 2.16 (s, $^3J_{Pt,H}$ = 25 Hz, 3 H, C-1–CH_3), 1.81 (s, $^3J_{Pt,H}$ = 35 Hz, 3 H, C-5–CH_3), 1.02 (s, $^2J_{Pt,H}$ = 76 Hz, 3 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ($CDCl_3$): δ = –3693 ppm. EI-MS: *m*/*z* = 461 [M]$^+$.

Synthesis of [(COD)Pt(R)(L)][PF_6]$_2$ (R = Bn or Me, L = MQ$^+$ or Mpz$^+$): [(COD)Pt(Bn)Cl] (488 mg, 1.135 mmol) or [(COD)Pt(Me)Cl] (401 mg, 1.135 mmol) was dissolved in acetone, and Ag[PF_6] (287 mg, 1.135 mmol) was added. Immediately, a colourless precipitate was observed; after 30 min, the reaction mixture was filtered, and the colourless filtrate was mixed with (MQ)[PF_6] (359 mg, 1.135 mmol) or (Mpz)[PF_6] (273 mg, 1.135 mmol). After stirring for 2 h, the reaction mixture was evacuated to dryness. Recrystallisation of the off-white residue from CH_2Cl_2 afforded the product.

[(COD)Pt(Bn)(MQ)][PF_6]$_2$: Colourless microcrystals (820 mg, 0.958 mmol, 84%). $C_{26}H_{30}F_{12}N_2P_2Pt$ (855.57): calcd. C 36.50, N 3.27, H 3.53; found C 36.64, N 3.30, H 3.59. ^{1}H NMR ([D_6]acetone): δ = 9.28 (d, 2 H, MQ 2-H, 6-H), 8.90 (d, 2 H, MQ 2′-H, 6′-H), 8.68 (d, 2 H, MQ 3-H, 5-H), 8.24 (d, 2 H, MQ 3′-H, 5′-H), 6.98–6.94 (m, 3 H, Bn 3-H, 4-H, 5-H), 6.82 (m, 2 H, Bn 2-H, 6-H), 5.52 (m, $^2J_{Pt,H}$ = 36 Hz, 2 H, COD 6-H), 5.47 (m, $^2J_{Pt,H}$ = 72 Hz, 2 H, COD 2-H) 4.70 (s, 3 H, CH_3), 3.03 (s, $^2J_{Pt,H}$ = 90 Hz, 2 H, PhCH_2) 2.86–2.50 (m, 8 H, COD CH_2) ppm. ^{195}Pt,^{1}H HMBC ([D_6]acetone): δ = –3670 ppm.

[(COD)Pt(Bn)(Mpz)][PF_6]$_2$: Colourless solid (796 mg, 1.021 mmol, 90%). $C_{20}H_{26}F_{12}N_2P_2Pt$ (779.45): calcd. C 30.82, N 3.59, H 3.36; found C 30.84, N 3.60, H 3.39. ^{1}H NMR ([D_6]acetone): δ = 9.68 (d, 2 H, Mpz 3-H, 5-H), 9.35 (d, 2 H, Mpz 2-, 6-H), 7.23–7.08 (m, 5 H, Bn ArH), 5.58 (m, $^2J_{Pt,H}$ = 36 Hz, 2 H, COD 2-H), 5.28 (m, $^2J_{Pt,H}$ = 85 Hz, 2 H, COD 6-H), 4.78 (s, 3 H, CH_3), 2.99 (s, $^2J_{Pt,H}$ = 85 Hz, 2 H, PhCH_2), 2.90–2.48 (m, 8 H, COD CH_2) ppm. ^{195}Pt,^{1}H HMBC ([D_6]acetone): δ = –3618 ppm.

[(COD)Pt(Me)(MQ)][PF_6]$_2$: Colourless solid (754 mg, 0.967 mmol, 85%). $C_{20}H_{26}F_{12}N_2P_2Pt$ (779.45): calcd. C 30.82, N 3.59, H 3.36; found C 30.80, N 3.57, H 3.34. ^{1}H NMR ([D_6]acetone): δ = 9.28 (d, 2 H, MQ 2-H, 6-H), 9.21 (d, 2 H, MQ 2′-H, 6′-H), 8.73 (d, 2 H, MQ 3-H, 5-H), 8.40 (d, 2 H, MQ 3′-H, 5′-H), 5.54 (m, $^2J_{Pt,H}$ = 30 Hz, 2 H, COD 6-H), 5.35 (m, $^2J_{Pt,H}$ = 78 Hz, 2 H, COD 2-H) 4.70 (s, 3 H, CH_3), 2.78–2.48 (m, 8 H, CH_2) 0.89 (s, $^2J_{Pt,H}$ = 69 Hz, 3 H, CH_3) ppm. ^{195}Pt,^{1}H HMBC ([D_6]acetone): δ = –3662 ppm.

Supporting Information (see footnote on the first page of this article): Tables containing crystallographic and structural data, figures showing the crystal and molecular structures.

Acknowledgments

The authors are indebted to Dr. Wieland Tyrra (University of Cologne) for NMR spectroscopy experiments. A donation of K_2PtCl_4 by Johnson Matthey, U.K. and financial support by the Deutsche Forschungsgemeinschaft (DFG) (KL 1194/11-1 to A. L. and A. K.) is gratefully acknowledged. V. L. acknowledges a grant from the Heinrich-Hertz-Stiftung.

[1] R. S. Nyholm, *Proc. Chem. Soc. London* **1961**, 273–296.
[2] R. S. Nyholm, *Pure Appl. Chem.* **1971**, *27*, 127–144.
[3] W. C. Zeise, *Ann. Phys. Chem.* **1831**, *97*, 497–541.
[4] a) M. Benedetti, C. R. Barone, D. Antonucci, V. M. Vechio, A. Ienco, L. Maresca, G. Natile, F. P. Fanizzi, *Dalton Trans.* **2012**, *41*, 3014–3021; b) P. B. Chock, J. Halpern, F. E. Paulik, S. I. Shupack, T. P. DeAngelis, *Inorg. Synth.* **1990**, *28*, 349–351; c) R. A. Love, T. F. Koetzle, R. Bau, *Inorg. Chem.* **1975**, *14*, 2653–2657; d) M. Black, R. H. B. Mais, P. G. Owston, *Acta Crystallogr., Sect. B* **1969**, *25*, 1753–1759; e) K. Birnbaum, *Ann. Chim. Farm.* **1869**, *152*, 137–147.
[5] L. B. Hunt, *Platinum Met. Rev.* **1984**, *28*, 76–83.
[6] a) R. I. McDonald, G. Liu, S. S. Stahl, *Chem. Rev.* **2011**, *111*, 2981–3019; b) R. Jira, *Angew. Chem. Int. Ed.* **2009**, *48*, 9034–9037; *Angew. Chem.* **2009**, *121*, 9196; c) J. A. Keith, P. M. Henry, *Angew. Chem. Int. Ed.* **2009**, *48*, 9038–9049; *Angew. Chem.* **2009**, *121*, 9200; d) L. Hintermann, *Wacker Oxidation*, in: *Handbook of C–H Transformations*, Wiley-VCH, Weinheim, Germany, **2005**, vol. 1, p. 287–301.
[7] a) N. M. Weliange, P. R. Sharp, *Organometallics* **2012**, *31*, 6823–6833; b) E. Szuromi, P. R. Sharp, *Organometallics* **2006**, *25*, 558–559; c) H. Shan, P. R. Sharp, *Inorg. Chem.* **1998**, *37*, 5727–5732.
[8] a) S. Komiya, I. Endo, *Chem. Lett.* **1988**, *13*, 1709–1712; b) S. Komiya, Y. Mizuno, T. Shibuya, *Chem. Lett.* **1986**, *15*, 1065–1068.
[9] a) S. Otto, *Inorg. Chim. Acta* **2010**, *363*, 3316–3320; b) D. C. Smith Jr., C. M. Haar, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1427–1433; c) R. Wyrwa, W. Poppitz, H. Görls, *Z. Anorg. Allg. Chem.* **1997**, *623*, 649–653.
[10] Y. Suzaki, K. Osakada, *Organometallics* **2004**, *23*, 5081–5084.
[11] a) Z. Dawoodi, C. Eaborn, A. Pidcock, *J. Organomet. Chem.* **1979**, *170*, 95–104; b) C. Eaborn, K. J. Odell, A. Pidcock, *J. Chem. Soc., Dalton Trans.* **1978**, 357–368.
[12] H.-A. Brune, R. Hohenadel, G. Schmidtberg, U. Ziegler, *J. Organomet. Chem.* **1991**, *402*, 179–199.
[13] a) A. Lüning, J. Schur, L. Hamel, I. Ott, A. Klein, *Organometallics* **2013**, *32*, 3662–3672; b) A. Klein, A. Lüning, I. Ott, L. Hamel, M. Neugebauer, K. Butsch, V. Lingen, F. Heinrich, S.

Elmas, *J. Organomet. Chem.* **2010**, *695*, 1898–1905; c) K. Butsch, S. Elmas, N. Sen Gupta, R. Gust, F. Heinrich, A. Klein, Y. von Mering, M. Neugebauer, I. Ott, M. Schäfer, H. Scherer, T. Schurr, *Organometallics* **2009**, *28*, 3906–3915; d) A. Klein, T. Schurr, H. Scherer, N. Sen Gupta, *Organometallics* **2007**, *26*, 230–233.

[14] a) J. van Slageren, A. Klein, S. Zalis, *Coord. Chem. Rev.* **2002**, *230*, 193–211; b) A. Klein, J. van Slageren, S. Zalis, *J. Organomet. Chem.* **2001**, *620*, 202–210; c) A. Klein, K.-W. Klinkhammer, T. Scheiring, *J. Organomet. Chem.* **1999**, *592*, 128–135.

[15] a) J. R. Berenguer, E. Lalinde, M. T. Moreno, *Coord. Chem. Rev.* **2010**, *254*, 832–875; b) A. Díez, E. Lalinde, M. T. Moreno, S. Sánchez, *Dalton Trans.* **2009**, 3434–3446; c) A. Díez, J. Fernandez, E. Lalinde, M. T. Moreno, S. Sánchez, *Dalton Trans.* **2008**, 4926–4936; d) J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, *Inorg. Chim. Acta* **2003**, *347*, 145–154; e) J. Forniés, A. García, J. Gómez, E. Lalinde, M. T. Moreno, *Organometallics* **2002**, *21*, 3733–3743; f) L. R. Falvello, S. Fernández, J. Forniés, E. Lalinde, F. Martínez, M. T. Moreno, *Organometallics* **1997**, *16*, 1326–1330.

[16] U. Belluco, R. Bertani, R. A. Michelin, M. J. Mozzon, *J. Organomet. Chem.* **2000**, *600*, 37–55.

[17] a) B. Wrackmeyer, B. Ullmann, R. Kempe, M. Herberhold, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2629–2634; b) M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2002**, *641*, 173–184.

[18] M. N. Jagadeesh, W. Thiel, J. Köhler, A. Fehn, *Organometallics* **2002**, *21*, 2076–2087.

[19] A. Sivaramakrishna, B. C. E. Makhubela, F. Zheng, H. Su, G. S. Smith, J. R. Moss, *Polyhedron* **2008**, *27*, 44–52.

[20] N. Oberbeckmann, K. Merz, R. A. Fischer, *Organometallics* **2001**, *20*, 3265–3273.

[21] a) Z. Wang, C. D. Abernethy, A. H. Cowley, J. N. Jones, R. A. Jones, C. L. B. Macdonald, L. Zhang, *J. Organomet. Chem.* **2003**, *666*, 35–42; b) T. Koizumi, T. Teratani, T. Yamamoto, *Inorg. Chem. Commun.* **2011**, *14*, 292–295; c) M. Hörner, G. Manzoni de Oliveira, J. Saldanha de Oliveira, W. M. Teles, C. A. L. Filgueiras, J. Beck, *J. Organomet. Chem.* **2006**, *691*, 251–254; d) M. B. Dinger, W. Henderson, *Chem. Commun.* **1996**, 211–212; e) J. C. Peters, S. B. Harkins, S. D. Brown, M. W. Day, *Inorg. Chem.* **2001**, *40*, 5083–5091; f) M. Fang, N. D. Jones, M. J. Ferguson, R. McDonald, R. G. Cavell, *Angew. Chem. Int. Ed.* **2005**, *44*, 2005–2008; *Angew. Chem.* **2005**, *117*, 2041.

[22] a) V. Lingen, A. Lüning, C. Strauß, I. Pantenburg, G. B. Deacon, G. Meyer, A. Klein, *Inorg. Chim. Acta* **2014**, *423*, 152–162; b) B. Rivera, H. Torrens, S. Bernès, *Acta Crystallogr., Sect. E* **2006**, *62*, m3287–m3288; c) J. García, E. Martin, D. Morales, H. Torrens, F. del Río, *Inorg. Chim. Acta* **1993**, *207*, 93–96; d) G. Rivera, S. Bernès, C. Rodriguez de Barbarin, H. Torrens, *Inorg. Chem.* **2001**, *40*, 5575–5580; e) S. D. Cummins, R. Eisenberg, *Inorg. Chem.* **1995**, *34*, 2007–2014.

[23] K. Osakada, T. Hosoda, T. Yamamoto, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 923–930.

[24] A. Fleischer, A. Roller, V. B. Arion, B. K. Keppler, F. Mohr, *Can. J. Chem.* **2009**, *87*, 146–150.

[25] a) J. Vicente, M. T. Chicote, C. MacBeath, J. Fernández-Baeza, D. Bautista, *Organometallics* **1999**, *18*, 2677–2682; b) S. J. Betts, A. Harris, R. N. Haszeldine, R. V. Parish, *J. Chem. Soc. A* **1971**, 3699–3705.

[26] W. N. O. Wylie, A. J. Lough, R. H. Morris, *Organometallics* **2010**, *29*, 570–581.

[27] J. L. Boyer, R. R. Cundari, N. J. deYonker, T. B. Rauchfuss, S. R. Wilson, *Inorg. Chem.* **2009**, *48*, 638–645.

[28] a) T. G. Appleton, R. D. Berry, J. R. Hall, D. W. Neale, *J. Organomet. Chem.* **1989**, *364*, 249–273; b) T. G. Appleton, J. R. Hall, M. A. Williams, *J. Organomet. Chem.* **1986**, *303*, 139–149; c) T. G. Appleton, J. R. Hall, D. W. Neale, M. A. Williams, *J. Organomet. Chem.* **1984**, *276*, C73–C76.

[29] J. L. Butikofer, J. M. Oerter, R. G. Peters, D. M. Roddick, *Organometallics* **2004**, *23*, 400–4008.

[30] a) E. E. Finney, R. G. Finke, *Inorg. Chim. Acta* **2006**, *359*, 2879–2887; b) P. Laurent, L. Veyre, C. Thieuleux, S. Donet, C. Coperet, *Dalton Trans.* **2013**, *42*, 238–248.

[31] a) M. Faust, M. Enders, K. Gao, L. Reichenbach, T. Muller, W. Gerlinger, B. Sachweh, G. Kasper, M. Bruns, S. Bräse, M. Seipenbusch, *Chem. Vap. Deposition* **2013**, *19*, 274–283; b) M. Faust, M. Enders, M. Bruns, S. Bräse, K. Gao, M. Seipenbusch, *Surf. Coat. Technol.* **2013**, *230*, 284–289; c) V. Aggarwal, L. R. Reichenbach, M. Enders, T. Muller, S. Wolff, M. Crone, M. Türk, S. Bräse, *Chem. Eur. J.* **2013**, *19*, 12794–12799; d) H. Gehrke, J. Pelka, C. G. Hartinger, H. Blank, F. Bleimund, R. Schneider, D. Gerthsen, S. Bräse, M. Crone, M. Türk, D. Marko, *Arch. Toxicol.* **2011**, *85*, 799–812; e) J. Pelka, H. Gehrke, M. Esselen, M. Türk, M. Crone, S. Bräse, T. Muller, H. Blank, W. Send, V. Zibat, P. Brenner, R. Schneider, D. Gerthsen, D. Marko, *Chem. Res. Toxicol.* **2009**, *22*, 649–659.

[32] a) C. Cullinane, G. B. Deacon, P. R. Drago, T. W. Hambley, K. T. Nelson, L. K. Webster, *J. Inorg. Biochem.* **2002**, *89*, 293–301; b) G. B. Deacon, B. M. Gatehouse, K. T. Nelson-Reed, *J. Organomet. Chem.* **1989**, *359*, 267–283; c) G. B. Deacon, K. T. Nelson-Reed, *J. Organomet. Chem.* **1987**, *322*, 257–268.

[33] a) B. C. Ankianiec, G. B. Young, *Polyhedron* **1995**, *14*, 249–265; b) B. C. Ankianiec, G. B. Young, *Polyhedron* **1991**, *10*, 1411–1421; c) B. C. Ankianiec, G. B. Young, *Polyhedron* **1989**, *8*, 57–69; d) S. K. Thomson, G. B. Young, *Polyhedron* **1988**, *7*, 1953–1964.

[34] a) T. G. Appleton, J. R. Hall, C. H. L. Kennard, M. T. Mathieson, D. W. Neale, G. Smith, T. C. W. Mak, *J. Organomet. Chem.* **1993**, *453*, 299–306; b) T. G. Appleton, J. R. Hall, M. T. Mathieson, D. W. Neale, *J. Organomet. Chem.* **1993**, *453*, 307–316.

[35] a) J. Vicente, A. Arcas, M.-D. Galvez-Lopez, P. G. Jones, D. Bautista, *Organometallics* **2009**, *28*, 3501–3517; b) J. Vicente, A. Arcas, J. M. Fernandez-Hernandez, G. Aullon, D. Bautista, *Organometallics* **2007**, *26*, 6155–6169.

[36] A. I. Zayya, J. L. Spencer, *Organometallics* **2012**, *31*, 2841–2853.

[37] a) G. Kickelbick, F. Stöhr, U. Schubert, *Acta Crystallogr., Sect. E* **2002**, *58*, m387–m388; b) J. Pfeiffer, G. Kickelbick, U. Schubert, *Organometallics* **2000**, *19*, 62–71.

[38] T. M. Miller, A. N. Izumi, Y.-S. Shih, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 3146–3156.

[39] a) J. Vicente, M. T. Chicote, C. MacBeath, *Organometallics* **2003**, *22*, 1843–1848; b) G. B. Deacon, P. R. Drago, D. Göbbels, M. S. Wickleder, G. Meyer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 811–813.

[40] a) A. De Renzi, R. Palumbo, G. Paiaro, *J. Am. Chem. Soc.* **1971**, *93*, 880–883; b) C. Pedone, E. Benedetti, *J. Organomet. Chem.* **1971**, *31*, 403–414.

[41] a) J. Reedijk, *Pure Appl. Chem.* **2011**, *83*, 1709–1719; b) F. Arnesano, G. Natile, *Coord. Chem. Rev.* **2009**, *253*, 2070–2081; c) J. Reedijk, *Eur. J. Inorg. Chem.* **2009**, 1303–1312; d) L. Kelland, *Nat. Rev. Cancer* **2007**, *7*, 573–584; e) S. J. Berners-Price, L. Ronconi, P. J. Sadler, *Prog. Nucl. Magn. Reson. Spectrosc.* **2006**, *49*, 65–98.

[42] a) T. C. Johnstone, G. Y. Park, S. J. Lippard, *Anticancer Res.* **2014**, *34*, 471–476; b) T. C. Johnstone, J. J. Wilson, S. J. Lippard, *Inorg. Chem.* **2013**, *52*, 12234–12249; c) J. J. Wilson, S. J. Lippard, *Chem. Rev.* **2013**, *114*, 4470–4495; d) N. Graf, S. J. Lippard, *Adv. Drug Delivery Rev.* **2012**, *64*, 993–1004; e) S. Dhar, S. J. Lippard, in: *Bioinorganic Medicinal Chemistry* (Ed.: E. Allesio), Wiley-VCH, Weinheim, Germany, **2011**, p. 79–96; f) K. S. Lovejoy, S. J. Lippard, *Dalton Trans.* **2009**, 10651–10659.

[43] M. Benedetti, D. Antonucci, D. Migoni, V. M. Vechio, C. Ducani, F. P. Fanizzi, *ChemMedChem* **2010**, *5*, 46–51.

[44] a) M. Enders, B. Görling, A. B. Braun, J. E. Seltenreich, L. F. Reichenbach, K. Rissanen, M. Nieger, B. Luy, U. Schepers, S. Bräse, *Organometallics* **2014**, *33*, 4027–4034.
[45] R. G. Denning, L. M. Venanzi, *J. Chem. Soc.* **1963**, 3241–3247.
[46] a) C. Kavakli, A. Gabrielsson, M. Sieger, B. Schwederski, M. Niemeyer, W. Kaim, *J. Organomet. Chem.* **2007**, *692*, 3151–3155; b) A.-R. Song, I.-C. Hwang, K. Ha, *Acta Crystallogr., Sect. E* **2007**, *63*, m2259; c) K. H. Ebert, W. Massa, H. Donath, J. Lorberth, B.-S. Seo, E. Herdtweck, *J. Organomet. Chem.* **1998**, *559*, 203–207; d) R. E. Rundle, J. H. Sturdivant, *J. Am. Chem. Soc.* **1947**, *69*, 1561–1567; e) W. J. Pope, S. J. Peachey, *J. Chem. Soc. Trans.* **1909**, *95*, 571–576.
[47] a) R. S. Pryadun, O. O. Gerlits, J. D. Atwood, *J. Coord. Chem.* **2006**, *59*, 85–100; b) J. R. Briggs, C. Crocker, W. S. McDonald, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1982**, 457–463.
[48] C. E. L. Headford, R. Mason, P. R. Ranatunge-Bandarage, B. H. Robinson, J. Simpson, *J. Chem. Soc., Chem. Commun.* **1990**, 601–603.
[49] a) T. G. Appleton, J. R. Hall, S. F. Ralph, *Inorg. Chem.* **1985**, *24*, 673–677; T. G. Appleton, J. R. Hall, S. F. Ralph, *Inorg. Chem.* **1985**, *24*, 4685–4693; b) H. Motschi, P. S. Pregosin, L. M. Venanzi, *Helv. Chim. Acta* **1979**, *62*, 667–677; c) P. S. Pregosin, H. Omura, L. M. Venanzi, *J. Am. Chem. Soc.* **1973**, *95*, 2047–2048; d) T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422.
[50] B. Still, P. G. A. Kumar, J. R. Aldrich-Wright, W. S. Price, *Chem. Soc. Rev.* **2007**, *36*, 665–686.
[51] L. Ronconi, P. J. Sadler, *Coord. Chem. Rev.* **2008**, *252*, 2239–2277.
[52] S. Schäfer, I. Ott, R. Gust, W. S. Sheldrick, *Eur. J. Inorg. Chem.* **2007**, 3034–3046.
[53] T. Koizumi, A. Yamazaki, T. Yamamoto, *Dalton Trans.* **2008**, 3949–3952, and references cited therein.
[54] *SHELXTL*, version 5.10, Bruker Analytical X-ray Systems Inc., Madison, **1997**.
[55] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122; b) L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838; c) G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, Universität Göttingen, Germany, **1997**.
[56] H. Scheffler, Y. You, I. Ott, *Polyhedron* **2010**, *29*, 66–69.
[57] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411–428.
[58] K. A. Jensen, *Acta Chem. Scand.* **1953**, *7*, 866–872.
[59] C. Eaborn, K. Kundu, A. Pidcock, *J. Chem. Soc., Dalton Trans.* **1981**, 933–938.
[60] D. B. Dell-Amico, L. Labella, F. Marchetti, S. Samaritani, *J. Organomet. Chem.* **2011**, *696*, 1349–1354.
[61] *Gmelin, Handbook: Pt*: *MVolD* **1990**, p. 440–441.
[62] R. J. Bertino, B. A. W. Coller, G. B. Deacon, I. K. Johnson, *J. Fluorine Chem.* **1975**, *5*, 335–357.
[63] R. J. Cross, M. F. Davidson, *J. Chem. Soc., Dalton Trans.* **1986**, 1987–1992.

Received: October 6, 2014
Published Online: November 24, 2014

