EPR study of electron transfer and group transfer in organoplatinum(II) and (IV) compounds †

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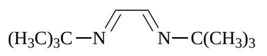
Chelate complexes between the 1,4-diazabuta-1,3-diene ligands RN=CH–CH=NR = R–DAB (R = alkyl, aryl) and the organoplatinum fragments $PtMe_2$, $PtMe_4$ and $PtMes_2$ (Mes = mesityl) can be reversibly reduced to paramagnetic compounds, formulated as platinum(II) or (IV) species bound by radical anion ligands (R-DAB$^{\cdot -}$). EPR studies in fluid and frozen solution support this assignment; however, the metal contribution to the singly occupied MO is higher for the paramagnetic Pt^{II} species than for the Pt^{IV} systems. Comparison with related radical complexes of the main group and transition element series reveals that even the organoplatinum(IV) compounds exhibit a relatively high degree of ligand-to-metal spin transfer as evident from small $^1H(CH)$ and large ^{14}N and ^{195}Pt EPR hyperfine coupling constants. The tetramethylplatinum(IV) complexes are photoreactive; a platinum-containing primary dissociation product from platinum–carbon σ bond homolysis has been detected by EPR spectroscopy using Bu^t-NO as a spin trap reagent during irradiation. Group transfer reactivity has also been noted for radical anions where the conversion $[(R\text{-DAB})PtMe_2]^{\cdot -} \longrightarrow [(R\text{-DAB})PtMe_4]^{\cdot -}$ could be monitored by EPR spectroscopy.

Platinum(II) and (IV) complexes with nitrogen donor-containing ligands have found interest as chemotherapeutic agents (cytostatica),[1] as catalysts,[2] and as photoemissive[3] or redox-active species.[4] The latter often involve π-accepting chelate ligands of the α-diimine type such as aromatic 2,2′-bipyridine[4c,f,i,j] or 1,10-phenanthrolines.[4g] Detailed photophysical studies,[3] calculations,[3d] structure determinations,[3c,d,4c,e] (spectro)electrochemical and EPR studies of generated paramagnetic species[4] have been used recently to elucidate the nature of these systems (L)-PtX_n in ground, reduced, oxidized and low-lying excited states.

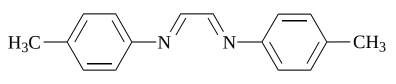
Considering the electronic complexity of these compounds[3,4] the use of organic substituents as co-ligands X seems attractive due to the great variability of such groups. For instance, the use of axially protecting mesityl (Mes, 2,4,6-trimethylphenyl) substituents in compounds (α-diimine)$PtMes_2$ has allowed us to avoid the undesired addition of nucleophiles to the one-electron oxidized monomeric platinum(III) states $[(\alpha\text{-diimine})PtMes_2]^+$.[4c,f] It was thus possible to obtain spectroelectrochemical data on monomeric organometallic Pt^{III} systems[4f] and to use the corresponding Pt^{II}/Pt^{III} half-wave potentials in correlations between optical data (absorption, emission energies) and electrochemical results.[4f]

Employing the smaller and simpler 1,4-diazabuta-1,3-dienes R-DAB as chelate ligands[5,6] instead of aromatic systems such as 2,2′-bipyridine we recently reported a first attempt to obtain a clearer picture of the electronic structure in these compounds.[4e] Smaller systems not only may provide less ambiguous experimental information, *e.g.* less spectral overlap,[4e] they are also better suited for theoretical access *via* quantum chemical calculations.[7] Furthermore, the variation of *N*-substituents[5,6] R from electron releasing alkyl to electron-accepting aryl groups, including axially shielding 2,6-dimethylphenyl substituents, should provide clues as to the electronic and/or steric effects governing the physical properties.

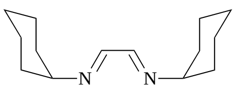
In the following we present results for organoplatinum complexes which contain R-DAB as chelating ‘non-innocent’ ligands.[5,6] Complexes of R-DAB have been widely used in coordination chemistry[5,6] and catalysis;[8] they have been considered ‘better’[6] π acceptors than 2,2′-bipyridine due to their lower-lying π* acceptor level and the higher MO coefficients at the coordinating nitrogen centers in that π* LUMO.



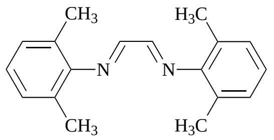
Bu^t-DAB



p-Tol-DAB



c-Hex-DAB



Xyl-DAB

Spectroscopy (UV–VIS, EPR), electrochemistry and the structure of complexes (c-Hex-DAB)$PtMe_n$, $n = 2,4$, have been reported.[4e] In this work we describe the EPR results obtained for electrogenerated species $[(R\text{-DAB})PtR'_n]^{\cdot -}$, involving the following compounds: (R-DAB)$PtMe_n$, $n = 2,4$; R = *tert*-butyl (Bu^t: **1a**,**b**), cyclohexyl (c-Hex: **2a**,**b**), *p*-tolyl (*p*-Tol: **3a**,**b**) and 2,6-dimethylphenyl (Xyl: **4a**,**b**); (*p*-Tol-DAB)$PtMes_2$ (**5**).

The methyl group (Me) as the simplest organic substituent and the mesityl function as an axially protecting aryl group[4c,f,9] were used as organic co-ligands at platinum. Details of UV–VIS spectroelectrochemical measurements will be published elsewhere.[7]

Considering the photolability of the tetramethylplatinum(IV) species[4e,10] we were also interested in studying the primary step of this photoreactivity. In agreement with previous concepts and interpretations of the photoreactivity of species (R-DAB)-MR'_n we may assume[11] the homolysis of one metal–(alkyl)-carbon bond, prompted by intramolecular electron transfer from the appropriate M–C σ combination (highest occupied

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Table 1 Electrochemical and EPR data of radical complexes $[(\text{R-DAB})\text{PtR}'_n]^{\bullet -}$ [a]

Radical		$E_{1/2(\text{red})}$/V	g_{iso} [b]	$a(^{195}\text{Pt})$ [c]	g components [d]				
					g_1	g_2	g_3	$A_1(^{195}\text{Pt})$	Δg [e]
$[(\text{R-DAB})\text{PtMe}_4]^{\bullet -}$									
R = Bu^t	**1b**	−1.98	1.9963	5.86 [f]	*g*				
c-Hex	**2b**	−1.93	1.9945	6.12 [h]	2.003	2.003	1.9976 [i]	7.5	0.0294
p-Tol	**3b**	−1.41	1.9958	5.90 [j]	2.0078	2.0035	1.9780 [k]	6.0	0.0298
Xyl	**4b**	−1.48	1.9943	6.26 [l]	*g*				
$[(\text{R-DAB})\text{PtMe}_2]^{\bullet -}$								$A_2(^{195}\text{Pt})$	
R = c-Hex	**2a**	−1.84	2.016	*m*	2.090 [n]	2.0163	1.944	6.5	0.146
p-Tol	**3a**	−1.36	2.021	*m*	*g*				
Xyl	**4a**	−1.53	2.078	*m*	2.105 [n]	2.012	1.941	6.3	0.164
$[(\text{R-DAB})\text{PtMes}_2]^{\bullet -}$								$A_2(^{195}\text{Pt})$	
R = *p*-Tol	**5**	−1.41	2.014	*m*	2.079 [n]	2.0065	1.958	5.8	0.121

[a] Redox potentials $E_{\frac{1}{2}}$ from cyclic voltammetry in acetonitrile–0.1 mol dm^{-3} Bu_4NPF_6. Potentials in V *vs.* ferrocene/ferrocenium, scan rate 100 mVs^{-1}. Radicals were generated from neutral precursors by *in situ* cathodic reduction in THF–0.1 mol dm^{-3} Bu_4NPF_6. [b] Isotropic *g* value, measured at 298 K in solution. [c] Isotropic coupling constant in mT for ^{195}Pt ($I = \frac{1}{2}$, 33.8% nat. abundance). [d] Measured in glassy frozen solutions at 110 K. [e] $\Delta g = g_1 - g_3$. [f] $a(^{14}\text{N}) = 0.87$ mT, $a(^1\text{H}) = 0.41$ mT. [g] Not available. [h] $a(^{14}\text{N}) = 0.82$ mT, $a(^1\text{H}) = 0.42$ mT. [i] A_3 (^{1}H) = 1.71 mT (septet 2 CH_3). [j] $a(^{14}\text{N}) = 0.80$ mT, $a(^1\text{H}) = 0.42$ mT. [k] $A_3(^1\text{H}) = 1.53$ mT (septet, 2 CH_3). [l] $a(^{14}\text{N}) = 0.79$ mT, $a(^1\text{H}) = 0.42$ mT. [m] <5 mT. [n] Measured at 3.3 K.

MO) to the π* level of R-DAB (lowest unoccupied MO).[11] Since the direct observation[11] of radical intermediates by EPR did not produce informative spectra, a spin trap reagent, Bu^t-NO,[12] was used to intercept the metal-containing intermediate of this homolysis.

Experimental

Syntheses

All preparations and physical measurements were carried out in dried solvents under an argon atmosphere, using Schlenk techniques. Furthermore, the tetramethylplatinum(IV) compounds had to be prepared and studied in the absence of intense light.

The preparation of compounds (c-Hex-DAB)PtMe$_n$, $n = 2,4$ (**2a**,**b**), has already been reported.[4e] The compounds (R-DAB)-PtMe$_n$, $n = 2,4$; R = Bu^t, c-Hex, *p*-Tol and Xyl were obtained accordingly from $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$[13] or $[\text{Pt}_2\text{Me}_8(\mu\text{-SMe}_2)_2]$[10] and appropriate 1,4-disubstituted 1,4-diazabuta-1,3-dienes,[14] the full characterisation by NMR and UV–VIS spectroscopy being described elsewhere.[7]

(*p*-Tol-DAB)PtMes$_2$ (**5**) was obtained by reacting 0.88 g (0.15 mmol) of $(\text{DMSO})_2\text{PtMes}_2$[15] (DMSO = dimethyl sulfoxide) and 40 mg (0.17 mmol) of *p*-Tol-DAB for 20 h in 20 cm^3 of refluxing toluene. Reducing the volume to one third and cooling to −30 °C yielded 52 mg (52%) of the dark-green product (correct C,H,N analysis).[7]

Instrumentation

EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. A two-electrode capillary (Pt)[16] was used for electrogeneration of radical complexes and a Bruker double cavity equipped with a shutter was employed for the photogeneration of radicals. The light source was a halogen lamp (100 W); cut-off filters were used optionally to exclude high energy radiation. Cyclic voltammetry was carried out in acetonitrile–0.1 mol dm^{-3} Bu_4NPF_6 using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple[17] served as internal reference.

Results and discussion

Reduction of complexes

All organoplatinum complexes (R-DAB)PtR′$_n$ described in this study are reduced reversibly in one-electron processes to yield paramagnetic radical anions. The reduction potentials and EPR data are summarised in Table 1; Figs. 1 and 2 illustrate representative EPR spectra of electrogenerated anions in fluid solution.

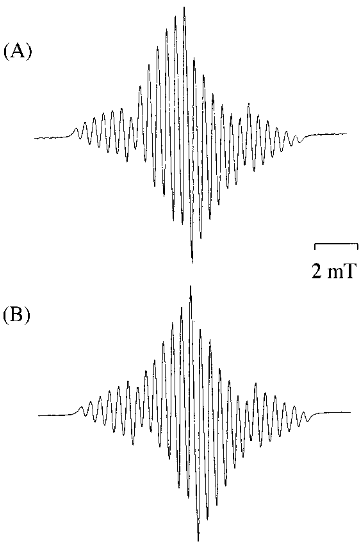


Fig. 1 (A) Experimental EPR spectrum of cathodically generated $[(\text{Bu}^t\text{-DAB})\text{PtMe}_4]^{\bullet -}$ (**1b**$^{\bullet -}$) in THF–0.1 mol dm^{-3} Bu_4NPF_6 at 298 K and (B) computer simulated spectrum with the values from Table 1 and 0.21 mT linewidth

The reduction potentials as measured in acetonitrile–0.1 mol dm^{-3} Bu_4NPF_6 reflect the substituent effect of the groups R at the nitrogen centers of the R-DAB ligands, pointing to a predominantly ligand-centered electron uptake. In agreement with standard organic concepts, the electron accepting aryl substituents facilitate reduction in comparison to exclusively electron-releasing alkyl substituents. Values in tetrahydrofuran (THF) solution (where the EPR measurements were carried out) are slightly more negative by about 0.1 V. As was pointed out previously,[4e] there is a surprising similarity of redox potentials between the dimethyl- and tetramethyl-platinum complexes of specific R-DAB ligands. Obviously, the change in metal oxidation state, from low-valent Pt$^{\text{II}}$ to more electron accepting Pt$^{\text{IV}}$, is exactly compensated by the strong σ donor effect of two additional carbanionic methyl substituents.

The EPR spectra of the complexes $[(\text{R-DAB})\text{PtR}'_n]^{\bullet -}$ in THF–0.1 mol dm^{-3} Bu_4NPF_6 exhibit different degrees of resol-

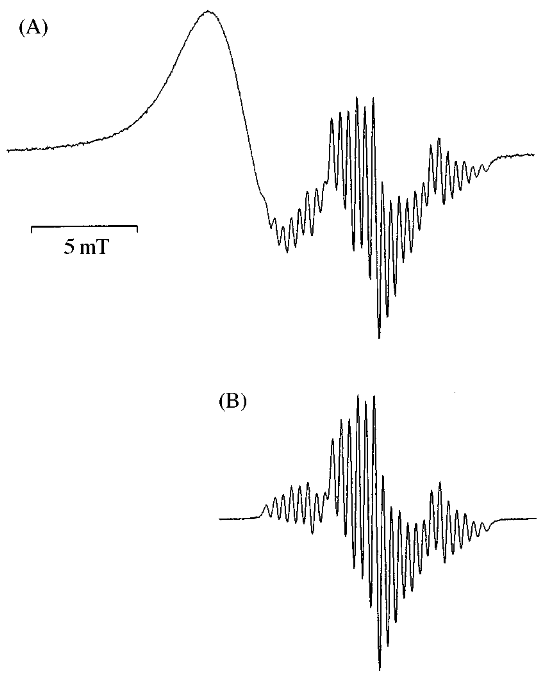


Fig. 2 (A) EPR spectra observed after electrochemical reduction of (Xyl-DAB)PtMe$_2$ (**4a**) in THF–0.1 mol dm^{-3} Bu$_4$NPF$_6$ at 298 K; (B) EPR spectrum of seperately generated [(Xyl–DAB)PtMe$_4$]$^{\bullet -}$ (**4b**$^{\bullet -}$) in THF–0.1 mol dm^{-3} Bu$_4$NPF$_6$ at 298 K

ution and different g factors. The tetramethylplatinum(IV) complexes display resolved hyperfine-structured EPR spectra (Figs. 1, 2) and have $g_{\mathrm{iso}} < g_{\mathrm{electron}} = 2.0023$ (Table 1). In contrast, the isotropic g values of the dimethyl- and dimesityl-platinum(II) compounds lie above g_{electron} (Table 1) and the spectra are not sufficiently resolved to detect any hyperfine coupling. In glassy frozen solution the Pt$^{\mathrm{II}}$ species are distinguished by a markedly higher g anisotropy as expressed by $\Delta g = g_1 - g_3$ (Table 1); also, the splitting of g components is more rhombic for the Pt$^{\mathrm{II}}$ and more axial for the Pt$^{\mathrm{IV}}$ anion radical compounds (Table 1).[4e]

All these differences between Pt$^{\mathrm{II}}$ and Pt$^{\mathrm{IV}}$ species point to a higher participation from the metal in the platinum(II) complexes, in spite of the very similar redox potentials; well resolved EPR spectra with hyperfine structuring as well as small axial g anisotropy are characteristic of compounds between diamagnetic metal complex fragments and radical ligands.[18]

The deviation of g from g_e also reflects the higher contribution from the heavy metal centre with its large spin orbit coupling constant.[18,19] Whereas the small decrease of g_{iso} for the d^6 systems [(R-DAB)Pt$^{\mathrm{IV}}$Me$_4$]$^{\bullet -}$ points to unoccupied MOs such as two unoccupied d orbitals lying close to the singly occupied MO, *i.e.* the π^* of R-DAB, the deviation to higher g_{iso} values for the diorganoplatinum compounds rather suggests little participation from a Pt$^{\mathrm{I}}$ formulation. A d^9 configuration is usually distinguished by $g > g_e$.[19,20]

$$[(\text{R-DAB}^{-\mathrm{I}})\text{Pt}^{\mathrm{II}}\text{R}_2]^{\bullet -} \longleftrightarrow [(\text{R-DAB}^{0})\text{Pt}^{\mathrm{I}}\text{Me}_2]^{\bullet -}$$

Unfortunately, the ligand and metal hyperfine features were not always detectable for the complexes [(R-DAB)PtR$_n$]$^{\bullet -}$, despite the small number of relevant nuclei and the large nuclear magnetic moment of the ^{195}Pt isotope (33.8% natural abundance, $I = 1/2$).[19] The room temperature EPR spectra of [(R-DAB)PtMe$_4$]$^{\bullet -}$ could be analysed, showing the expected[21–25] ^{14}N and ^{1}H hyperfine splitting from the coordinated R-DAB radical anion and the platinum hyperfine coupling as 'triplet' satellite lines (Fig. 1).[4] In glassy frozen solution, the Pt$^{\mathrm{IV}}$ species show metal hyperfine features a_1(Pt) and a septet structure $a_3{}^{4e}$ which we tentatively attribute to the axial methyl groups (hyperconjugative spin transfer). The paramagnetic Pt$^{\mathrm{II}}$ complexes show a clear ^{195}Pt splitting for the central g component (Table 1) and a quintet splitting $a_3{}^{4e}$ which is tentatively assigned to the ^{14}N nuclei of the R-DAB ligand.

Table 2 EPR data of 1,4-diazabutadiene radical complexes [(Bu^t-DAB)ML$_n$]$^{\bullet -\,a}$

ML$_n$	$a(^1\mathrm{H})$/mT	$a(^{14}\mathrm{N})$/mT	a(M)/mT	a(M)/10$^{-3}A_{\mathrm{iso}}{}^b$
ZnMe$^{+\,c}$	0.585	0.485	*d*	
ZnMe$_2{}^e$	0.552	0.552	0.179 (^{67}Zn)	3.94
AlEt$_2{}^{+\,f}$	0.536	0.537	0.792 (^{27}Al)	8.06
MgCl$^{+\,g}$	0.53	0.53	0.096 (^{25}Mg)	8.07
Re(CO)$_3{}^{+\,h}$	0.465	0.726	3.561 (^{185,187}Re)	11.05
K$^{+\,i}$	0.437	0.562	*d*	
Mn(CO)$_3{}^{+\,h}$	0.435	0.748	0.847 (^{55}Mn)	7.75
Mo(CO)$_4{}^i$	0.42	0.707	0.29 (^{95,97}Mo)	6.16
PtMe$_4$	0.41	0.87	5.86 (^{195}Pt)	15.80

[a] Coupling constants a in mT. [b] Isotropic coupling constants A_{iso} from ref. 19. [c] Generated by thermolysis in THF at 300 K (ref. 21). [d] Not detected. [e] Generated photochemically in n-hexane by irradiation at $\lambda > 550$ nm (ref. 21). [f] Generated by thermolysis in n-pentane at 293 K (ref. 22). [g] Ref. 23. [h] In benzene or toluene, generated photochemically at $\lambda > 320$ nm (ref. 24). [i] Generated by chemical reduction with potassium in 1,2-dimethoxyethane (DME) at 293 K (ref. 25).

The hyperfine data from well-resolved room temperature EPR spectra of complexes [(R-DAB)PtMe$_4$]$^{\bullet -}$ can be put into perspective by comparison with several other radical species [(R-DAB)ML$_n$]$^{\bullet -}$, R = Bu^t (Table 2).[21–25]

The data from Table 2 illustrate the special position of the tetramethylplatinum(IV) fragment, the radical anion complex showing the smallest proton and largest ^{14}N hyperfine coupling of the R-DAB ligand and the largest ratio $a(\mathrm{M})/A_{\mathrm{iso}}(\mathrm{M})$ where A_{iso} is the isotropic hyperfine coupling constant.[19] This trend signifies a fairly large amount of ligand-to-metal spin transfer already for the Pt$^{\mathrm{IV}}$ derivative; the EPR data for the Pt$^{\mathrm{II}}$ species suggest an even higher degree of spin delocalization there. Metal contributions to the SOMO in the order of a few percent were calculated for platinum(II) complexes of the α-diimine anion radical ligands.[4i–k]

An initially puzzling result was observed when the complexes (R-DAB)PtMe$_2$, R = p-Tol, Xyl, were reduced at room temperature. In addition to the broad unresolved EPR signal of the parent radical anions [(R-DAB)PtMe$_2$]$^{\bullet -}$ a second well-resolved spectrum appeared which could be assigned to [(R-DAB)PtMe$_4$]$^{\bullet -}$ (Fig. 2). This seemingly paradoxical oxidation (Pt$^{\mathrm{II}} \longrightarrow$ Pt$^{\mathrm{IV}}$) under reducing conditions can be attributed to an established kind of reactivity of such compounds [(α-diimine)MR$_n$]$^{\bullet -}$, *i.e.* group transfer capability.[26] In analogy to similar reactivity of organozinc complexes[21,26] of R-DAB ligands we tentatively formulate a methyl group transfer to the coordinatively unsaturated radical anion [(R-DAB)PtMe$_2$]$^{\bullet -}$ to account for the observed spectroscopic phenomena (Fig. 2).

Spin-trapping of radicals following photoinduced Pt–C bond homolysis

The tetramethylplatinum(IV) complexes (R-DAB)PtMe$_4$ are photosensitive, especially in the dissolved state. While the final, diamagnetic products originating from that photoreactivity will be described elsewhere,[7] we can address here the question of the primary photoprocesses. We have previously interpreted the photoreactivity of species (R-DAB)MR′$_n$ in terms of an intramolecular electron transfer from an M–C σ combination (HOMO) to the π^* level of R-DAB (LUMO) which then results in the homolysis of one metal–(alkyl)carbon bond.[11,21]

In the case of organozinc complexes with R-DAB ligands in particular it was possible to directly observe[21] thermally or photolytically generated radical intermediates with well resolved EPR spectra. *In situ* irradiation of complexes (R-DAB)-PtMe$_4$ in diethyl ether at temperatures between 160 and 230 K produced only weak, broad EPR signals centered around

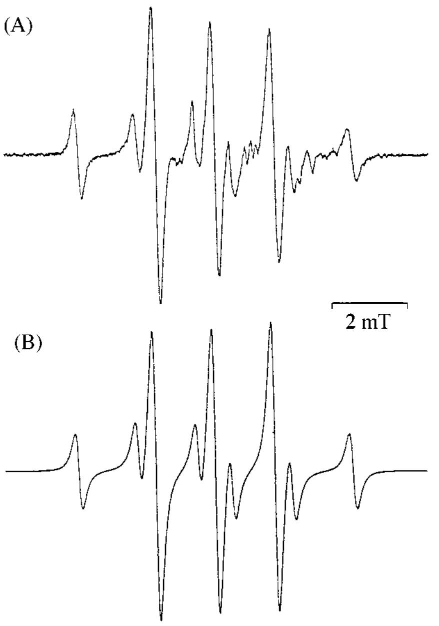
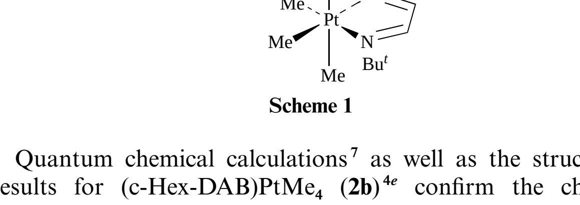


Fig. 3 (A) Experimental EPR spectrum of the radical obtained after irradiating (Bu^t-DAB)$\mathrm{PtMe_4}$ (**1b**) at 240 K in diethyl ether in the presence of Bu^t-NO with a halogen lamp; (B) computer simulated spectrum with $a(^{14}\mathrm{N}) = 1.58$ mT, $a(^{195}\mathrm{Pt}) = 4.0$ mT and 0.26 mT linewidth

$g = 2.00$ with unresolved or insufficiently resolved hyperfine features. Visible light ($\lambda > 515$ nm) was sufficient to induce photoreactivity. To obtain better spectral information the spin trap reagent 2-methyl-2-nitrosopropane, Bu^t-NO,[12] was used to intercept at least one of the intermediates of the assumed homolysis; Fig. 3 shows the spectrum obtained.

In situ irradiation of (Bu^t-DAB)$\mathrm{PtMe_4}$ (**1b**) at 240 K in diethyl ether gave a nitrosyl species with the typical[12] $a(^{14}\mathrm{N})$ value of 1.56 mT and a $^{195}\mathrm{Pt}$ satellite splitting of 4.0 mT (Fig. 3). The g factor of 2.0060 is clearly influenced by the high spin–orbit coupling constant of platinum. Both the g and the $a(^{195}\mathrm{Pt})$ value suggest that the spin trap has intercepted the organometallic part of the assumed photoinduced Pt–$\mathrm{C_{ax}}$ bond homolysis (Scheme 1).



Scheme 1

Quantum chemical calculations[7] as well as the structural results for (c-Hex-DAB)$\mathrm{PtMe_4}$ (**2b**)[4e] confirm the chelate coordination of an essentially unperturbed 1,4-diazabuta-1,3-diene conjugated system and the significantly longer metal-to-carbon bonds to the axial methyl groups (2.140 Å) than to the equatorial $\mathrm{CH_3}$ substituents (2.045 Å). This difference is larger than the one observed for complexes (dmpe)$\mathrm{MnMe_4}$ or (dmpe)-$\mathrm{TiMe_4}$ [dmpe = 1,2-bis(dimethylphosphino)ethane].[27] We thus postulate the homolysis of a metal-to-carbon bond in the axial position after irradiation into long-wavelength bands. Incidentally, it may be interesting to note that the photolability of neutral complexes such as (L)$\mathrm{Mn(CO)_2(C_5R_5)}$ or (L)$\mathrm{Mo(CO)_2(PR_3)_2}$ and now (L)$\mathrm{PtMe_4}$ is often paralleled by low isotropic g values of the corresponding radical anions, close-lying unoccupied orbitals being responsible for both effects.[28,29]

Acknowledgements

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References

1 (*a*) N. Farrell in *Transition Metal Complexes as Drugs and Chemotherapeutic Agents*, ed. B. R. James and R. Ugo, Reidel-Kluwer, Dordrecht, The Netherlands, 1989, p. 46; (*b*) M. J. Bloemink and J. Reedijk, in *Metal Ions in Biological Systems*, vol. 32, ed. H. Sigel and A. Sigel, Marcel Dekker, Inc., New York, 1996, p. 641; (*c*) W. I. Sundquist and S. J. Lippard, *Coord. Chem. Rev.*, 1990, **100**, 293.

2 (*a*) S. S. Stahl, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1996, **118**, 5961; (*b*) M. W. Holtcamp, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1997, **119**, 848.

3 (*a*) V. M. Miskowski and V. H. Houlding, *Inorg. Chem.*, 1989, **28**, 1529; (*b*) C.-M. Che, L.-Y. He, C.-K. Poon and C. W. Mak, *Inorg. Chem.*, 1989, **28**, 3081; (*c*) J. Biedermann, G. Gliemann, U. Klement, K.-J. Range and M. Zabel, *Inorg. Chem.*, 1990, **29**, 1884; (*d*) J. Biedermann, G. Gliemann, U. Klement, K.-J. Range and M. Zabel, *Inorg. Chim. Acta*, 1990, **169**, 63; (*e*) H. Kunkely and A. Vogler, *J. Am. Chem. Soc.*, 1990, **112**, 5625; (*f*) V. M. Miskowski and V. H. Houlding, *Inorg. Chem.*, 1991, **30**, 4446; (*g*) L. Chassot and A. von Zelewsky, *Helv. Chim. Acta*, 1986, **69**, 1855; (*h*) V. M. Miskowski, V. H. Houlding, C. M. Che and Y. Wang, *Inorg. Chem.*, 1993, **32**, 2518; (*i*) V. H. Houlding and V. M. Miskowski, *Coord. Chem. Rev.*, 1991, **111**, 145; (*j*) C. Cornioley-Deuschel and A. von Zelewsky, *Inorg. Chem.*, 1987, **26**, 3354; (*k*) A. von Zelewsky, P. Belser, P. Hayoz, R. Dux, X. Husa, A. Suckling and H. Stoeckli-Evans, *Coord. Chem. Rev.*, 1994, 75; (*l*) C.-W. Chan, L.-K. Cheng and C.-M. Che, *Coord. Chem. Rev.*, 1994, **132**, 87; (*m*) S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 1949; (*n*) C. S. Peyratout, T. K. Aldridge, D. K. Crites and D. R. McMillin, *Inorg. Chem.*, 1995, **34**, 4484; (*o*) W. B. Connick, L. M. Henling, R. E. Marsh and H. B. Gray, *Inorg. Chem.*, 1996, **35**, 6261.

4 (*a*) P. S. Braterman, J.-I. Song, C. Vogler and W. Kaim, *Inorg. Chem.*, 1992, **31**, 222; (*b*) C. Vogler, B. Schwederski, A. Klein and W. Kaim, *J. Organomet. Chem.*, 1992, **436**, 367; (*c*) A. Klein, H.-D. Hausen and W. Kaim, *J. Organomet. Chem.*, 1992, **440**, 207; (*d*) P. S. Braterman, J.-I. Song, F. M. Wimmer, S. Wimmer, W. Kaim, A. Klein and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 5084; (*e*) S. Hasenzahl, H.-D. Hausen and W. Kaim, *Chem. Eur. J.*, 1995, **1**, 95; (*f*) W. Kaim and A. Klein, *Organometallics*, 1995, **14**, 1176; (*g*) A. Klein, W. Kaim, E. Waldhör and H.-D. Hausen, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2121; (*h*) R. J. Klinger, R. J. Huffman and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 2147; (*i*) S. A. MacGregor, E. McInnes, R. J. Sorbie and L. J. Yellowlees, in *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*, ed. A. J. L. Pombeiro and J. A. McCleverty, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993, p. 503; (*j*) D. Collison, F. E. Mabbs, E. J. L. McInnes, K. J. Taylor, A. J. Welch and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1996, 329; (*k*) M. G. Hill, J. A. Bailey, V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1996, **35**, 4585; (*l*) E. J. L. McInnes, A. J. Welch and L. J. Yellowlees, *J. Chem. Soc., Chem. Commun.*, 1996, 2393; (*m*) A. Klein, W. Kaim, J. Fiedler and S. Zalis, *Inorg. Chim. Acta*, in the press.

5 (*a*) G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151; (*b*) K. Vrieze and G. van Koten, *Inorg. Chim. Acta*, 1985, **100**, 79.

6 H. tom Dieck, K.-D. Franz and F. Hohmann, *Chem. Ber.*, 1975, **108**, 163.

7 S. Hasenzahl, A. Klein, W. Kaim, H. Stoll, S. Zalis and J. Fiedler, submitted to *Organometallics*.

8 L. Deng, P. Margl and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 1094.

9 (*a*) W. Kaim and A. Schulz, *Angew. Chem.*, 1984, **96**, 611; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 615; (*b*) A. Schulz and W. Kaim, *Chem. Ber.*, 1989, **122**, 1863; (*c*) A. Lichtblau, W. Kaim, A. Schulz and T. Stahl, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1497.

10 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.

11 (*a*) W. Kaim, *Top. Curr. Chem.*, 1994, **169**, 231; (*b*) S. Hasenzahl, W. Kaim and T. Stahl, *Inorg. Chim. Acta*, 1994, **225**, 23.

12 (*a*) G. G. Janzen, *Acc. Chem. Res.*, 1971, **4**, 31; (*b*) C. A. Evans, *Aldrichim. Acta*, 1979, **12**, 23.

13 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1986, **5**, 1538.

14 (*a*) H. tom Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 92; (*b*) H. tom Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch.*, *Teil B*, 1981, **36**, 823.

15 C. Eaborn, K. Kundu and A. Pidcock, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 933.

16 W. Kaim, S. Ernst and V. Kasack, *J. Am. Chem. Soc.*, 1990, **112**, 173.

17 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

18 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187 and literature cited.

19 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

20 M. Symons, *Electron Spin Resonance Spectroscopy*, Van Nostrand Reinhold Comp., New York, 1978.

21 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606.

22 G. van Koten, J. T. B. H. Jastrzebski and K. Vrieze, *J. Organomet. Chem.*, 1983, **250**, 46.

23 P. Clopath and A. v. Zelewsky, *Helv. Chim. Acta*, 1972, **55**, 52.

24 R. R. Andrea, W. G. J. de Lange, T. van der Graf, M. Rijkhoff, D. J. Stufkens and A. Oskam, *Organometallics*, 1988, **7**, 1100.

25 K. D. Franz, H. tom Dieck. U. Krynitz and I. W. Renk, *J. Organomet. Chem.*, 1974, **64**, 361.

26 E. Wissing, S. van der Linden, E. Rijnberg, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1994, **12**, 2602.

27 (*a*) C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 1163; (*b*) K.-H. Thiele, H. Windisch, H. Schumann and G. Kociok-Köhn, *Z. Anorg. Allg. Chem.*, 1994, **620**, 523.

28 W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov and E. K. H. Roth, *J. Am. Chem. Soc.*, 1992, **114**, 5693.

29 S. Ernst, S. Kohlmann and W. Kaim, *J. Organomet. Chem.*, 1988, **354**, 177.

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