Reactivity of 4-Nitrosoanilines Towards Dimeric Halogenido-bridged Complexes of Iridium(III) and Rhodium(III) of the Type $[(\eta^5\text{-}C_5Me_5)MX_2]_2$

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

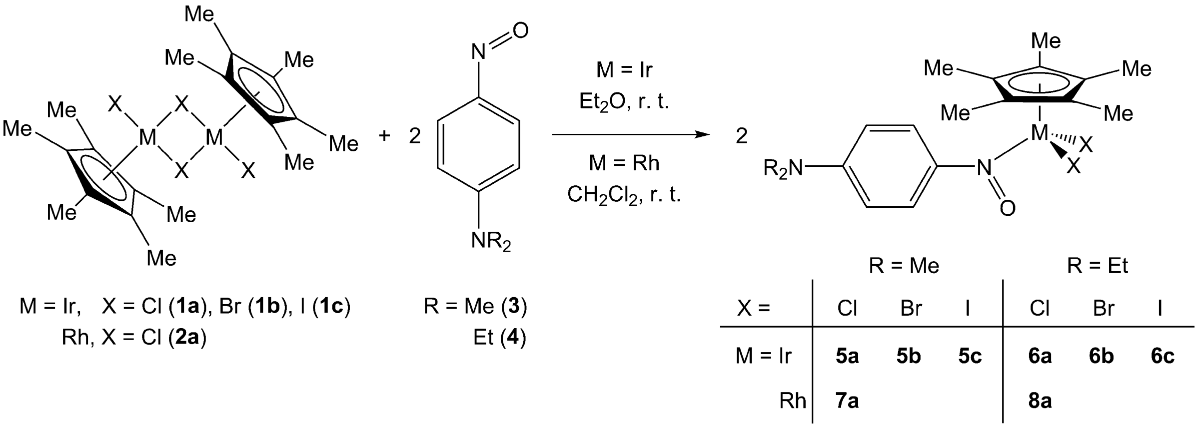
The synthesis, spectroscopic characterization and crystal structures of new *C*-nitrosoaryl complexes of iridium(III) and rhodium(III) are reported. The reactions of the μ_2-halogenido-bridged dimers $[(\eta^5\text{-}C_5Me_5)IrX_2]_2$ [X = Cl (**1a**), Br (**1b**), I (**1c**)] and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**2a**) with *N*,*N*-dimethyl- (**3**) and *N*,*N*-diethyl-4-nitrosoaniline (**4**) yield the mononuclear complexes $[(\eta^5\text{-}C_5Me_5)MX_2(\mathbf{3})]$ [M = Ir, X = Cl (**5a**), Br (**5b**), I (**5c**); M = Rh, X = Cl (**7a**)] and $[(\eta^5\text{-}C_5Me_5)MX_2(\mathbf{4})]$ [M = Ir, X = Cl (**6a**), Br (**6b**), I (**6c**); M = Rh, X = Cl (**8a**)]. All new compounds were characterized by their melting points, NMR, IR and mass spectra as well as in selected cases by UV/Vis spectroscopy. The X-ray structure analyses revealed a slightly distorted pseudo-octahedral configuration ("three-legged pianostool") and σ-*N* coordination of the *C*-nitroso ligand.

Key words: *C*-Nitroso Anilines, N Ligand, Iridium, Rhodium

Introduction

Aromatic compounds containing a *C*-nitroso group have been known for over 130 years. The first examples were already published in 1874 by A. von Bayer [1 – 3]. However, coordination to metal centers was not reported before 1907 [4]. Since these early attempts various synthetic routes to high-yield preparations of *C*-nitroso compounds were developed [5, 6]. Current reviews show the constant interest in this field of research during the last decades [7]. Not only due to its rich coordination chemistry with eleven different main coordination modes to metal centers [8, 9], the family of *C*-nitroso compounds has been investigated extensively. Also the possible applications in organic synthesis [10], for example the nitroso *ene* [11] or nitroso Diels-Alder reaction [12 – 14] attracted attention. The most important properties of the NO function for these applications are the high reactivity based upon the polarization of the N–O bond and the specific structure in the equilibrium between nitroso monomer and azodioxy dimer which leads to a unique chemo- and regioselectivity [10]. Since the discovery of the important roles of *C*-nitroso derivatives in various biological processes [15 – 23], their significance is also affirmed in biochemistry.

This article now is concerned with the coordination of *N*,*N*-dimethyl-4-nitrosoaniline (**3**) and *N*,*N*-diethyl-4-nitrosoaniline (**4**) to Ir(III) and Rh(III) complexes. These aromatic *C*-nitroso compounds show remarkably high reactivity because the amino group in *para*-position increases the electron density at the NO function [24]. Complexes containing these ligands are known for different metal centers and coordination modes as published by our group [25, 26] and others [8, 9]. However, examples for these or comparable aromatic *C*-nitroso ligands coordinated to Ir or Rh centers are rare in literature [27 – 39]. Besides our own results [36], the available crystallographic data for monodentate σ-*N*-coordination is limited to only two Rh(I) complexes [30, 32]. In fact, the new complexes presented in the following are the results of preliminary research to our recently published work on 1,4-bis(4-nitrosophenyl)piperazine as a bridging ligand [36] and are the only further examples for crystallographically characterized Ir(III) and Rh(III) complexes containing monodentate σ-*N*-coordinated aromatic *C*-nitroso ligands.



	R = Me			R = Et		
X =	Cl	Br	I	Cl	Br	I
M = Ir	**5a**	**5b**	**5c**	**6a**	**6b**	**6c**
Rh	**7a**			**8a**		

Scheme 1. Synthesis of the new iridium(III) (**5a**–**c**, **6a**–**c**) and rhodium(III) (**7a**, **8a**) complexes with **3** or **4** as ligands.

Results and Discussion

The new mononuclear complexes [(η^5-C$_5$Me$_5$)MX$_2$(**3**)] [M = Ir, X = Cl (**5a**), Br (**5b**), I (**5c**); M = Rh, X = Cl (**7a**)] and [(η^5-C$_5$Me$_5$)MX$_2$(**4**)] [M = Ir, X = Cl (**6a**), Br (**6b**), I (**6c**); M = Rh, X = Cl (**8a**)] are obtained as illustrated in Scheme 1. Addition of excess *N*,*N*-dimethyl-4-nitrosoaniline (**3**) or *N*,*N*-diethyl-4-nitrosoaniline (**4**) to the μ_2-halogenido-bridged Ir(III) (**1a-c**) or Rh(III) (**2a**) dimers in Et$_2$O or CH$_2$Cl$_2$, respectively, leads to their nucleophilic cleavage and yields the monosubstituted products. These are obtained as red (**5a**, **6a**, **7a**, **8a**) or green (**5b**, **5c**, **6b**, **6c**) microcrystalline solids and are stable when exposed to air. They show good solubility for instance in dichloromethane or chloroform and are insoluble in *n*-pentane.

Mass spectra of the iridium(III) complexes **5a**–**c** and **6a**–**c** in (+)-FAB mode exhibit the parent peak [M]$^+$ as well as a similar fragmentation resulting from the loss of the halogenido and nitroso ligands. Mass spectra ((+)-FAB mode) of the rhodium(III) compounds **7a** and **8a** lack the [M]$^+$ peak, but show also the typical fragmentation pattern starting with [M-Cl]$^+$.

In the ^{1}H NMR spectra of **5a**–**8a** the *N*-alkyl substituents are detected at the same positions as measured for the uncoordinated ligands (*N*-Me: 3.14(s) ppm; *N*-Et: 1.26 (t), 3.47(q) ppm). The signal of the Cp-methyl groups of **5a**–**8a** is located in the range of 1.52 – 1.82 ppm and shows a weak coordination-induced shift (0.05 – 0.10 ppm) to higher field compared to the starting complexes **1a**–**2a**. Due to rotation about the N2–C4 bond the proton signals of the aromatic ring are observed relatively broad; in particular for the protons in *ortho*-position of the nitroso group (H3, H5; 7.91 – 9.02 ppm) they are stretched at room temperature over a range of nearly 1.0 ppm. "Freezing" the rotation by a measurement at −60 °C leads to a significant splitting of the broad signal (**5c**: 7.24 and 9.01 ppm; $\Delta = 1.77$ ppm) as depicted for **5c** in Fig. 1 (A, B). This splitting is induced by the large magnetic anisotropy of the NO group and known for aromatic nitroso compounds [40, 41]. The peak at 9.01 ppm is clearly ascribed to the "*anti*-position" of the nitroso-O atom (H5) because of the strong deshielding effect of the functional group for this proton [41]. Similar effects appear in the ^{13}C NMR spectra of **5a**–**8a**. The carbons in *ortho*-position of the nitroso group (C3, C5; about 132 ppm) are observed as extremely broad signals for the iridium(III) complexes (**5a**–**c**, **6a**–**c**) and are not detectable for the rhodium(III) compounds (**7a**, **8a**). Again, in low temperature measurements (−60 °C) this very broad signal splits (**5c**: 122.6 and 140.9 ppm; $\Delta = 18.3$ ppm), and additionally even the peaks for C2 and C6 are separated (**5c**: 108.1 and 112.2 ppm; $\Delta = 4.1$ ppm) (Fig. 1: C, D). In both cases the signal found at lower field of each pair is ascribed to the deshielded *anti*-position to N = O [41]. Assignment of the peak in the range of 162.7 – 164.5 ppm to C4 (ON-C$_q$) and the one at about 155 ppm to C1 (N-C$_q$) was done according to Gowenlock *et al.* [42 – 44]. All other carbon signals are observed within the expected ranges.

In the IR spectra of **5a**–**8a** weak ν(C-H) absorptions are detected in the range of 3100 – 2800 cm^{-1} for all complexes. Within the fingerprint area (wavenum-

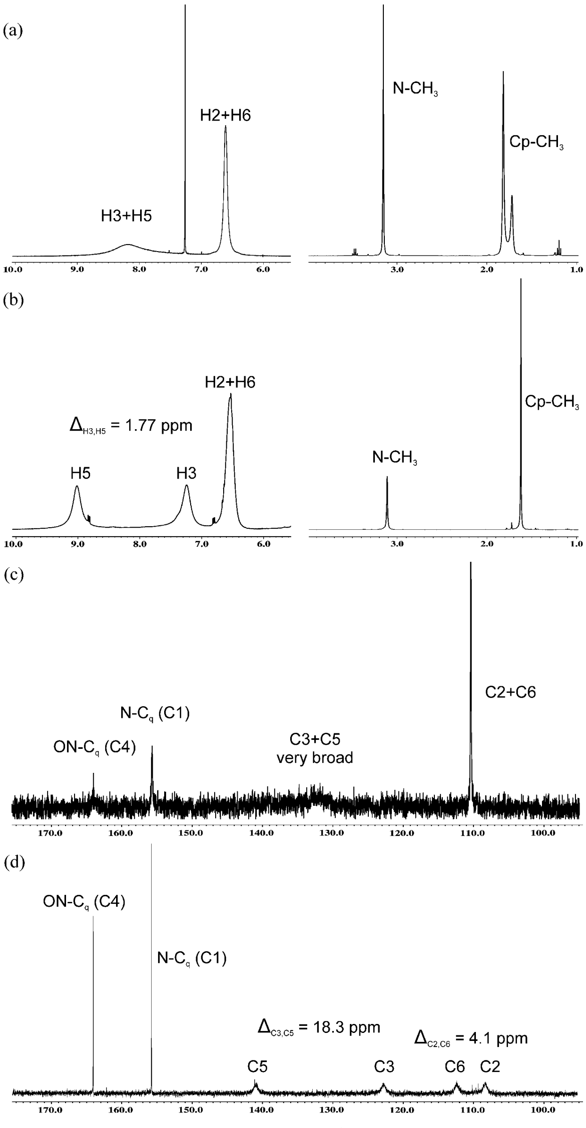


Fig. 1. Significant areas of the ^{1}H NMR (a: $CDCl_3$, b: CD_2Cl_2) and ^{13}C NMR spectra (c: $CDCl_3$, d: CD_2Cl_2) of **5c** at room temperature (a, c) and at −60 °C (b, d).

Table 1. UV/Vis absorption data of the ligands **3** and **4** and the complexes **5a**, **5b** and **6a** in CH_2Cl_2: λ_{max} (in nm), ε (in $L\,mol^{-1}\,cm^{-1}$) in parentheses.

	$\lambda_{max\,1}$	$\lambda_{max\,2}$	$\lambda_{max\,3}$
3	273 (6000)	420 (31 300)	–
5a	271 (5400)	420 (11 800)	509^{a} (19 000)
5b	273 (8000)	419 (21 900)	516^{a} (15 300)
4	274 (6300)	424 (32 600)	–
6a	270 (6500)	425 (15 400)	512^{a} (21 400)

[a] Weak shoulder at about 650 nm with no distinct maximum.

bers smaller than 1604 cm^{-1}) the $\nu(N=O)$ absorptions are assigned according to the literature value of **3** (1363 cm^{-1} [9, 45]; own equipment: CH_2Cl_2: 1365 cm^{-1}; ATR: 1362 cm^{-1}) to bands in the range of 1367 – 1361 cm^{-1} for **5a**–**c** and **7a**. For the complexes containing *N*,*N*-diethyl-4-nitrosoaniline (**6a**–**c**, **8a**) only a slight shift of the $\nu(N=O)$ absorption to lower frequencies is observed compared to literature data for the uncoordinated ligand (1380 cm^{-1} [46]; own equipment: CH_2Cl_2: 1377 cm^{-1}; ATR: 1370 cm^{-1}). The $\nu(N=O)$ band is found in the range of 1380 – 1369 cm^{-1} in CH_2Cl_2 solution and within 1366 – 1356 cm^{-1} for ATR measurement. This only small decrease in wavenumbers lies in the expected range for σ-*N* coordination of *C*-nitroso compounds [9, 47].

On account of the intense red color of the products in solution, UV/Vis spectra of **5a**, **5b** and **6a** in dichloromethane were recorded (Table 1). Two of the absorptions are already observed in the ligand spectra and show no significant shift in wavelength. $\lambda_{max\,1}$ is ascribed to a π-π^* absorption of the nitroso aniline and keeps its intensity after coordination. By contrast, $\lambda_{max\,2}$ looses intensity, as it originates from an intramolecular CT absorption of this “push-pull” ligand. The third band is tentatively ascribed to a ligand-to-metal CT absorption of the type [ON-Ir/Rh^{III}] (Ir/Rh^{III} is low-spin $t_{2g}{}^6$) and shows a weak shoulder at about 650 nm (most likely n-π^*) with no distinct maximum.

Single crystals suitable for X-ray diffraction analysis were obtained by slow isothermic diffusion of *n*-pentane into solutions of the complexes in chloroform (**5a**, **6a**, **6b**, **7a**, **8a**) or dichloromethane (**5c**, **6c**). Selected bond lengths and angles are listed and compared with those of ligands **3** [48] and **4** [46] in Table 2. Crystallographic data and details of the structure refinements are summarized in Table 3. Only two of the complexes are depicted as examples with atom numbering in Figures 2 (**6a**) and 3 (**7a**). The coordination sphere (“three-legged pianostool”) of each metal center consists of one pentamethyl-η^5-cyclopentadienyl, two terminal halogenido ligands and the σ-*N*-coordinated nitroso ligand. The M–X bond lengths in **5a**–**8a** are slightly longer than those found for the terminal halogenido ligands in the starting complexes (**1a**: 2.387(4) Å [49]; **1b**: 2.5195(2) Å [50];

Table 2. Selected bond lengths (Å) and angles (deg) of the ligands **3** [48] and **4** [46] and the complexes **5a**, **5c**, **6a–c**, **7a** and **8a**.

					Bond lengths					
	M-X1	M-X2	M-N2	O1-N2	N2-C4	N1-C1	C2-C3	C5-C6	C1-C2	C3-C4
3[a,b,c]	–	–	–	1.131	1.390	1.365	1.370	1.325	1.434	1.425
	–	–	–	1.121	1.390	1.365	1.325	1.370	1.394	1.362
	–	–	–	1.212	1.445	1.322	1.357	1.352	1.387	1.380
	–	–	–	1.292	1.445	1.322	1.352	1.357	1.444	1.402
5a	2.3952(1)	2.4121(1)	2.073(3)	1.255(4)	1.391(2)	1.347(2)	1.354(2)	1.357(6)	1.418(2)	1.424(2)
5c	2.7143(2)	2.7018(4)	2.069(2)	1.248(4)	1.385(3)	1.342(3)	1.366(9)	1.369(9)	1.446(9)	1.401(3)
7a	2.3980(6)	2.4172(6)	2.1069(18)	1.250(2)	1.390(3)	1.340(3)	1.363(3)	1.366(3)	1.428(3)	1.411(3)
4[a]	–	–	–	1.253[d]	1.438[d]	1.358(4)	1.376(2)	1.375(2)	1.420(2)	1.386(2)
	–	–	–	1.215[d]	1.458[d]	1.345(4)	1.372(2)	1.360(2)	1.425(2)	1.393(2)
6a[a]	2.3989(1)	2.4099(1)	2.068(3)	1.246(4)	1.391(2)	1.355(4)	1.356(2)	1.367(2)	1.418(2)	1.407(2)
	2.4026(1)	2.4145(1)	2.087(3)	1.252(4)	1.385(4)	1.348(2)	1.350(2)	1.369(2)	1.426(2)	1.419(2)
6b	2.5307(4)	2.5267(4)	2.054(2)	1.263(6)	1.382(4)	1.354(4)	1.356(3)	1.368(4)	1.432(3)	1.403(3)
6c	2.7061(4)	2.7026(4)	2.058(4)	1.254(2)	1.388(6)	1.341(6)	1.365(4)	1.348(4)	1.420(4)	1.399(4)
8a	2.5328(13)	2.5275(12)	2.086(3)	1.243(1)	1.363(11)	1.346(12)	1.404(13)	1.339(12)	1.419(13)	1.378(5)

	Angles							Torsion angles	
	X1-M-X2	N2-M-X1	N2-M-X2	O1-N2-M	O1-N2-C4	N2-C4-C3	C1-N1-C7	O1-N2-C4-C3	C7-N1-C1-C6
3[a,b,e]	–	–	–	–	126.2	116.5	123.1	–	–
	–	–	–	–	115.2	125.2	117.6	–	–
	–	–	–	–	116.4	121.3	121.5	–	–
	–	–	–	–	116.2	120.2	125.3	–	–
5a	87.57(4)	87.03(9)	94.85(9)	116.5(2)	116.1(3)	120.6(3)	121.9(3)	5.5(2)	0.8(6)
5c	90.369(5)	88.81(14)	91.84(14)	117.9(4)	114.7(2)	120.8(2)	121.0(6)	2.0(9)	−1.7
7a	89.71(2)	87.99(2)	96.36(2)	115.44(13)	116.01(17)	121.15(19)	121.48(19)	4.1(3)	0.4(3)
4[a,d]	–	–	–	–	110.85	128.64	122.66	−0.25	−4.67
	–	–	–	–	109.87	128.79	121.25	−2.45	3.69
6a[a]	85.07(4)	85.88(9)	92.13(9)	116.4(2)	115.8(3)	120.9(3)	121.8(3)	8.7(2)	1.5(6)
	85.87(4)	86.26(3)	92.56(3)	115.5(2)	115.7(3)	120.9(3)	121.4(4)	−7.4	11.8(6)
6b	88.53(3)	86.53(13)	88.53(3)	116.4(4)	115.0(2)	121.0(2)	122.4(2)	−7.4	2.9(9)
6c	89.367(14)	87.26(11)	94.28(12)	116.8(3)	115.4(4)	120.9(4)	122.1(4)	−10.5	2.8(3)
8a	88.58(2)	85.4(2)	92.8(2)	115.7(6)	115.9(3)	120.8(9)	121.2(9)	−11.4	6.8(5)

[a] Two molecular units in the unit cell. Column headings derived from the "first" fragment; from the "second" comparable data are given; [b] disorder of the nitroso group; [c] estimated standard deviations: 0.008–0.015 Å; [d] data obtained from the CCDC, standard deviations not available; [e] estimated standard deviations: 0.5 – 1.0°.

1c: 2.694(1) Å [50]; **2a**: 2.397(2) Å [51]). All angles enclosed by the halogenido ligands or by one halogenido and the nitroso ligand differ only by a few degrees from 90° (Table 2; only exception **7a**: N2–M–X2) and prove the only slight distortion of the *pseudo*-octahedral geometry. The Ir–N bonds observed in **5a**, **5c** and **6a–c** are in the range 2.054(2)-2.087(3) Å and therefore somewhat longer than reported for 1-chloro-2-nitroso-1,2-dihydrodicyclopentadiene σ-*N* coordinated to Ir(III) (1.948(6) Å) [52], but similar to that of our own recently published dinuclear Ir(III) complexes (2.061(4)-2.088(3) Å) [36]. Crystallographic data for *C*-nitroso ligands with σ-*N* coordination to Rh(III) are not available from other groups. Structure determinations are only known for ligand **3** (Rh–N 2.050(4) Å) [32] or 1-bromo-4-nitrosobenzene (Rh–N 1.958(3) Å) [30] at Rh(I) centers. Again the Rh–N bond lengths observed in **7a** (2.1069(18) Å) and **8a** (2.086(3) Å) are slightly longer and in good accordance to our results for 1,4-*bis*(4-nitrosophenyl)piperazin (2.097(2) Å) [36]. Thus, the M–N bond lengths found in **5a**–**8a** are close to those observed in Rh(III) or Ir(III) complexes with bidentate sp^2-*N*-donor ligands [53 – 57]. Due to the limited quality of the structural data of ligand **3** the obtained complexes are better compared with ligand **4** (although both ligand data sets are listed in Table 2). A comparison shows that there are only minor structural changes within the ligands after coordination. The N = O bond length is only marginally increased, and the quinoid

Table 3. Crystal data and details of structural refinement on **5a**, **5c**, **6a**-**c**, **7a** and **8a**.

Compound	**5a**	**5c**	**6a**	**6b**	**6c**	**7a**	**8a**[a]
Formula	$C_{18}H_{25}Cl_2IrN_2O$	$C_{18}H_{25}I_2IrN_2O$	$C_{20}H_{29}Cl_2IrN_2O$, $CHCl_3$	$C_{20}H_{29}Br_2IrN_2O$	$C_{20}H_{29}I_2IrN_2O$	$C_{18}H_{25}Cl_2N_2ORh$	$C_{20}H_{29}Cl_2N_2ORh$
F_W, g mol^{-1}	548.526	731.430	695.956	665.482	759.483	459.215	487.268
Crystal color, shape	black, platelet	red, platelet	brown, block	black, block	black, block	red, platelet	green, block
Crystal size, mm^3	0.13 × 0.11 × 0.02	0.12 × 0.12 × 0.02	0.14 × 0.13 × 0.06	0.13 × 0.11 × 0.05	0.14 × 0.13 × 0.08	0.16 × 0.09 × 0.04	0.11 × 0.08 × 0.07
T, K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group (no.)	$P2_1/c$(14)	$P\bar{1}$(2)	$P2_1/c$(14)	$Pbca$ (61)	$Pbca$ (61)	$P2_1/c$(14)	$Pbca$ (61)
a, Å	14.6792(3)	7.9489(3)	23.4790(2)	14.2625(3)	17.7739(4)	14.6636(3)	14.2612(2)
b, Å	7.55950(1)	9.0509(3)	8.5038(2)	17.7027(4)	14.6803(4)	7.5147(2)	17.7004(2)
c, Å	17.2526(3)	15.9243(2)	32.6240(1)	17.8783(3)	18.2883(2)	17.3496(2)	17.8728(3)
α, deg	90	78.1970(18)	90	90	90	90	90
β, deg	100.0729(13)	78.244(2)	128.011(2)	90	90	100.2936(12)	90
γ, deg	90	67.4651(18)	90	90	90	90	90
V, Å^3	1.93290(2)	1025.81(6)	5132.1(2)	4514.00(16)	4771.9(2)	1881.03(4)	4511.61(11)
Z	4	2	8	8	8	4	8
ρ_c, g cm^{-1}	1.93	2.37	1.80	1.96	2.11	1.62	1.43
μ, mm^{-1}	7.7	9.5	5.7	9.5	8.2	1.2	1.0
F(000), e	1064	676	2720	2544	2832	936	2000
θ range, deg	3.18–27.48	3.26–26.99	3.17–27.50	3.24–27.00	3.20–25.34	3.19–27.49	3.28–25.00
Index range	$-18 \le h \le 19$, $-9 \le k \le 9$, $-22 \le l \le 22$	$-10 \le h \le 10$, $-11 \le k \le 10$, $-20 \le l \le 20$	$-30 \le h \le 30$, $-11 \le k \le 11$, $-42 \le l \le 42$	$-18 \le h \le 18$, $-22 \le k \le 22$, $-22 \le l \le 22$	$-21 \le h \le 19$, $-16 \le k \le 17$, $-22 \le l \le 22$	$-18 \le h \le 19$, $-9 \le k \le 9$, $-22 \le l \le 22$	$-16 \le h \le 16$, $-20 \le k \le 21$, $-21 \le l \le 21$
Refls. collected/indep./	8218/4314/	8456/4456/	22 600/11 737/	9317/4912/	28 920/4350/	8226/4298/	7457/3941/
R_{int}	0.0350	0.0446	0.0337	0.0369	0.0617	0.0150	0.0125
Completeness to θ, %	99.7	99.5	99.7	99.8	99.6	99.4	99.4
Data/restraints/parameters	4314/0/224	4456/0/224	11737/0/563	4912/0/242	4350/0/242	4298/0/224	3941/0/243
Final R_1/wR_2 [$I > 2\sigma(I)$]	0.0263/0.1082	0.0396/0.0936	0.0300/0.0672	0.0375/0.0861	0.0290/0.0644	0.0257/0.0624	0.0643/0.1875
Final R_1/wR_2 (all data)	0.0368/0.0641	0.0477/0.0988	0.0434/0.0721	0.0676/0.0978	0.0412/0.0701	0.0313/0.0654	0.0717/0.1981
S on F^2	1.037	1.045	1.058	1.024	1.117	1.080	1.026
Largest diff. peak/hole, e Å^{-3}	1.491/ – 1.303	2.302/ – 1.944	1.117/ – 1.259	1.387/ – 1.258	1.844/ – 0.937	0.680/ – 0.620	1.872/ – 0.945
CCDC number	881 822	881 823	881 824	881 825	881 826	881 827	881 828

[a] The structure determination of **8a** was added as proof of the coordination but should not be used for a detailed discussion of the bond lengths and angels because the final refinement (see $wR2$ values) was relatively poor.

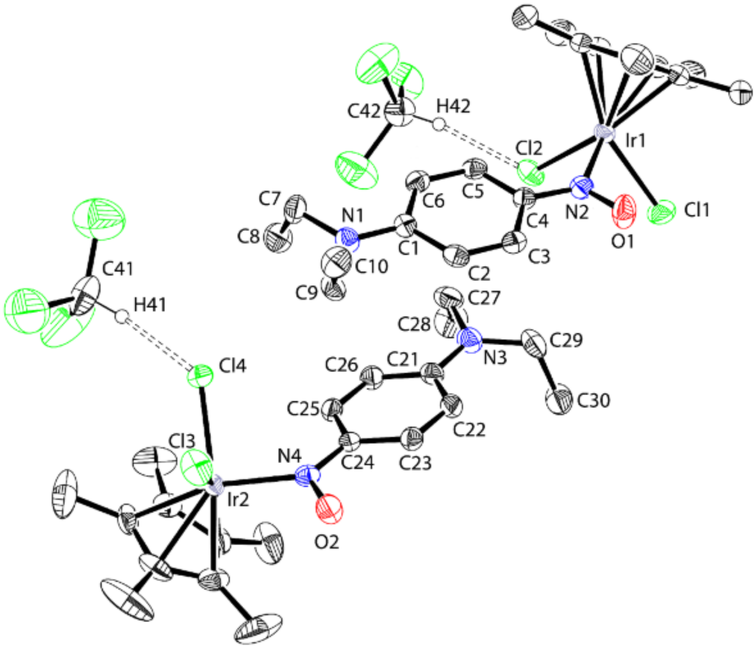


Fig. 2. Molecular structure of the iridium(III) complex **6a** with hydrogen bonds (dashed) to the next solvent molecules. The displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except $CHCl_3$) are omitted for clarity. Hydrogen bond data: C(41)–H(41)···Cl(4): d(D–H) 0.99(6), d(H···A) 2.47(4), d(D···A) 3.427(2), <(D–H–A) 162 (2)°; C(42)–H(42)···Cl(2)#1: d(D–H) 1.08(2), d(H···A) 2.38(2), d(D···A) 3.456(2), <(D–H–A) 175 (4)°; symmetry operator: #1 $x, -y+1/2, z+1/2$.

contribution to the aromatic ring is stronger. This is indicated by shorter N2–C4 and C2–C3 bonds and elongated C3–C4 bond lengths (Table 2). In all new complexes the NO function as well as the alkyl groups are located within the phenyl plane with only small deviations. It should be mentioned that the ethyl groups show the sterically preferred *trans*-configuration in uncoordinated **4** and in **6b**, **6c** and **8a**. In the crystal structure of **6a** embedded $CHCl_3$ leads to a relatively small intermolecular distance and *cis*-configuration of the ethyl groups of one of the two complex molecules in the asymmetric unit (Fig. 2).

Conclusion

In this paper we have presented the synthesis, spectroscopic properties and X-ray structures of new iridium(III) and rhodium(III) complexes containing *N*,*N*-dialkyl-4-nitrosoanilines (alkyl = methyl, ethyl) as monodentate σ-*N* ligands. NMR studies indicate that the well known NO rotation for *C*-nitroso compounds persists for these complexes in solution at room temperature, although the crystallographic characterization proves that the quinoid contribution to the aromatic ring of both *N*,*N*-dialkyl-4-nitrosoanilines is even increased after coordination. These interesting spectroscopic properties and the high reactivity of these ligands induced by the amino group in *para*-position to the NO function makes them promising candidates for the cleavage of many other halogenido or analogously bridged transition metal complexes.

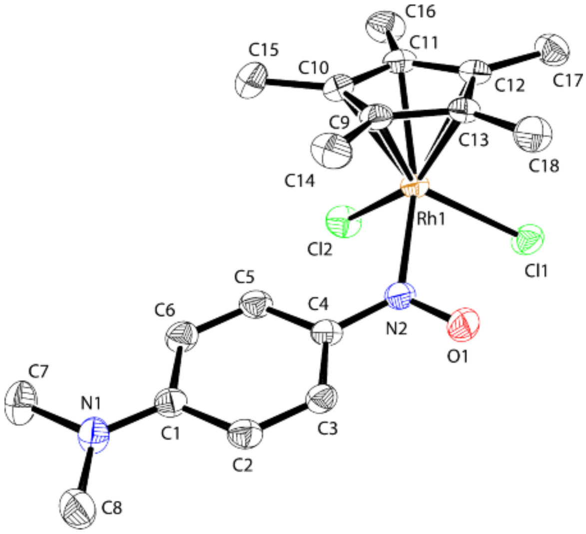


Fig. 3. Molecular structure of the rhodium(III) complex **7a**. The displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Experimental

General

All experiments for the preparation of the new complexes were performed under dry argon atmosphere using Schlenk and vacuum-line techniques. The starting complexes $[(\eta^5\text{-}C_5Me_5)IrX_2]_2$ (X = Cl (**1a**) [58], Br (**1b**) [59], I (**1c**) [60]) and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**2a**) [60] were prepared according to literature methods. *N*,*N*-Dimethyl-4-nitrosoaniline (**3**) and *N*,*N*-diethyl-4-nitrosoaniline (**4**) were commercially available and used as purchased. Solvents were purified by standard procedures; dichloromethane was distilled from calcium hydride, diethyl ether from sodium pieces and *n*-pentane from lithium aluminum hydride. Chloroform was dried dynamically in a column with 3 Å molecular sieves. All dried solvents were stored under dry argon atmosphere with 3 Å molecular sieves (chloroform, dichloromethane) or sodium pieces (diethyl ether, *n*-pentane).

Melting points were determined using a Büchi Melting-Point B-540 apparatus and are uncorrected. UV/Vis data were recorded with a Perkin Elmer Lambda 16 instrument in CH_2Cl_2 in the range of 250 – 800 nm. IR spectra were measured in the range of 4000 – 400 cm^{-1}; in solution with a Perkin Elmer Spectrum One FT-IR spectrometer and in the solid state using a Jasco FT/IR-460*Plus* instrument equipped with MIRacle^{TM} ATR (diamond cell) from PIKE Technologies. NMR spectra were obtained with Jeol Ecplise 270, Jeol Ecplise 400 and Jeol EX 400 spectrometers at ambient temperature unless stated otherwise. All chemical shifts δ are given in parts per million (ppm) relative to TMS. Mass spectra were obtained with a Jeol MStation JMS-700 in (+)-FAB mode with NBA (3-nitrobenzyl alcohol) matrix. Multi-isotopic fragments are referred to the isotope with the highest abundance. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry using a Heareus elementar varioEL instrument.

*Synthesis of the iridium(III) complexes **5a–c** and **6a–c***

The dimers $[(\eta^5\text{-}C_5Me_5)IrX_2]_2$ [X = Cl (**1a**), Br (**1b**), I (**1c**)] and six equivalents of ligand **3** or **4** were dissolved in 50 mL of dry Et_2O and stirred at room temperature. The solvent showed a dark-red color instantly. After the reaction was completed (see time below) the precipitate was filtered off and washed with dry Et_2O several times (till the filtrate is nearly colorless) to remove excess ligand. The resulting product was dried *in vacuo* for 12 h at 50 °C.

*(4-Nitroso-N,N-dimethylaniline-N)dichlorido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**5a**)*

Reagents: 122 mg (0.153 mmol) **1a**, 138 mg (0.918 mmol) **3**. Reaction time: 3 h. Yield: 162 mg (0.295 mmol, 96 %) dark-red microcrystalline solid. Black crystals (platelets) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **5a** in $CHCl_3$. M. p. decomp. > 206 °C. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 271 (5400), 420 (11 800), 509 nm (19 000 L mol^{-1} cm^{-1}). – IR (CH_2Cl_2): ν = 3051 (w), 2980 (w), 2924 (w), 2864 (w), 1601 (vs), 1554 (w), 1536 (w), 1442 (w), 1395 (w), 1382 (w), 1367 ν(N = O) (m), 1338 (m), 1310 (m), 1247 (m), 1137 (vs), 1029 (m), 989 (w), 940 (w), 877 (w), 827 (m), 632 (w), 611 (m), 592 (w) cm^{-1}. – IR (ATR, solid): ν = 3047 (w), 2985 (w), 2962 (w), 2918 (w), 2853 (w), 1596 (s), 1536 (w), 1479 (w), 1445 (w), 1393 (w), 1383(w), 1362 ν(N = O) (w), 1332 (s), 1308 (s), 1245 (s), 1224 (w), 1129 (vs), 1082 (w), 1034 (m), 1022 (m), 989 (w), 935 (w), 872 (m), 831 (s), 792 (w), 737 (s), 628 (w), 608 (m), 590 (m) cm^{-1}. – ^{1}H NMR (399.78 MHz, $CDCl_3$): δ = 1.52 (s, 15 H, Cp-C*H*$_3$), 3.14 (s, 6 H, N-C*H*$_3$), 6.53 (d, 2 H, ^3J = 9.67 Hz, C*H*$_{arom}$/H2+H6), 8.26 (br, 2 H, C*H*$_{arom}$/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 9.0 (Cp-*C*H$_3$), 41.2 (N-CH$_3$), 88.1 (Cp-*C*$_q$), 111.0 (*C*H$_{arom}$/C2+C6), 131.8 (br, *C*H$_{arom}$/C3+C5), 156.5 (N-*C*$_q$/C1), 164.0 (ON-*C*$_q$/C4). – MS ((+)-FAB): *m*/*z* (%) = 549.8 (4) [M]$^+$, 513.5 (28) [M-Cl]$^+$, 363.4 (100) [M-Cl-**3**]$^+$. – $C_{18}H_{25}Cl_2IrN_2O$ (548.53): calcd. C 39.41, H 4.59, N 5.11; found C 39.04, H 4.46, N 4.92.

*(4-Nitroso-N,N-dimethylaniline-N)dibromido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**5b**)*

Reagents: 145 mg (0.149 mmol) **1b**, 134 mg (0.894 mmol) **3**. Reaction time: 2 h. Yield: 123 mg (0.193 mmol, 65 %) dark-green microcrystalline solid. M. p. decomp. > 202 °C. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 273 (8000), 419 (21 900), 516 nm (15 300 L mol^{-1} cm^{-1}). – IR (CH_2Cl_2): ν = 3051 (w), 2978 (w), 2921 (w), 2864 (w), 1601 (vs), 1556 (w), 1537 (m), 1442 (w), 1394 (w), 1383 (w), 1367 ν(N = O) (m), 1337 (m), 1310 (m), 1245 (m), 1135 (vs), 1029 (m), 989 (w), 940 (w), 877 (m), 827 (m), 632 (w), 611 (m), 594 (w) cm^{-1}. – IR (ATR, solid): ν = 3055 (w), 2984 (w), 2962 (w), 2915 (w), 2854 (w), 1595 (s), 1542 (w), 1534 (w), 1483 (w), 1444 (w), 1393 (w), 1380(w), 1361 ν(N = O) (w), 1331 (s), 1307 (s), 1242 (s), 1226 (w), 1123 (vs), 1079 (w), 1032 (w), 1019 (m), 989 (w), 937 (m), 871 (m), 828 (s), 792 (w), 738 (s), 629 (m), 609 (m), 589 (m) cm^{-1}. – ^{1}H NMR (399.78 MHz, $CDCl_3$): δ = 1.58 (s, 15 H, Cp-C*H*$_3$), 3.14 (s, 6 H, N-C*H*$_3$), 6.54 (d, 2 H, ^3J = 9.35 Hz, C*H*$_{arom}$/H2+H6), 8.24 (br, 2 H, C*H*$_{arom}$/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 9.4 (Cp-*C*H$_3$), 41.1 (N-*C*H$_3$), 89.0 (Cp-*C*$_q$), 110.7 (*C*H$_{arom}$/C2+C6), 132.0 (br, *C*H$_{arom}$/C3+C5), 156.3 (N-*C*$_q$/C1), 164.5 (ON-*C*$_q$/C4). – MS ((+)-FAB): *m*/*z* (%) = 636.9 (9) [M]$^+$, 557.0 (86) [M-Br]$^+$, 477.1 (24) [M-2Br]$^+$, 407.1 (100) [M-Br-**3**]$^+$. – $C_{18}H_{25}Br_2IrN_2O$(637.43): calcd. C 33.92, H 3.95, N 4.39; found C 34.33, H 3.98, N 4.45.

*(4-Nitroso-N,N-dimethylaniline-N)diiodido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**5c**)*

Reagents: 216 mg (0.186 mmol) **1c**, 168 mg (1.116 mmol) **3**. Reaction time: 5 h. Yield: 246 mg (0.336 mmol, 90 %) dark-green microcrystalline solid. Red crystals (platelets) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **5c** in CH_2Cl_2. M. p. decomp. > 182 °C. – IR (CH_2Cl_2): ν = 3044 (w), 2975 (w), 2916 (w), 2864 (w), 1600 (vs), 1557 (w), 1532 (m), 1443 (w), 1393 (w), 1382 (w), 1366 $\nu(N=O)$ (m), 1338 (m), 1308 (m), 1240 (m), 1126 (vs), 1027 (m), 960 (w), 941 (w), 876 (w), 826 (m), 632 (w), 610 (m), 594 (w) cm^{-1}. – IR (ATR, solid): ν = 3069 (w), 2986 (w), 2954 (w), 2910 (w), 2851 (w), 1594 (s), 1541 (w), 1534 (w), 1484 (w), 1439 (w), 1391 (m), 1377 (w), 1361 $\nu(N=O)$ (w), 1329 (s), 1305 (s), 1229 (s), 1222 (w), 1121 (vs), 1074 (w), 1024 (m), 1017 (m), 988 (w), 936 (m), 873 (m), 824 (s), 789 (w), 736 (s), 628 (m), 614 (m), 608 (m), 594 (m) cm^{-1}. – ^1H NMR (399.78 MHz, $CDCl_3$): δ = 1.72 (s, 6 H, Cp-CH_3), 1.82 (s, 9 H, Cp-CH_3), 3.15 (s, 6 H, N-CH_3), 6.61 (br, 2 H, CH_{arom}/H2+H6), 8.18 (br, 2 H, CH_{arom}/H3+H5). – ^1H NMR (400.18 MHz, CD_2Cl_2, −60 °C): δ = 1.62 (s, 15 H, Cp-CH_3), 3.11 (s, 6 H, N-CH_3), 6.54 (br, 2 H, CH_{arom}/H2+H6), 7.24 (br, 1 H, CH_{arom}/H3), 9.01 (br, 1 H, CH_{arom}/H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 10.5 (Cp-CH_3), 10.9 (Cp-CH_3), 40.8 (N-CH_3), 89.0 (Cp-C_q), 90.3 ($C_{q,\,arom}$), 110.3 (CH_{arom}/C2+C6), 132.0 (br, CH_{arom}/C3+C5), 155.6 (N-C_q/C1), 164.0 (ON-C_q/C4). – ^{13}C NMR (100.63 MHz, CD_2Cl_2, −60 °C): δ = 9.6 (Cp-CH_3), 41.1 (N-CH_3), 89.2 (Cp-C_q), 108.1 (CH_{arom}/C2), 112.2 (CH_{arom}/C6), 122.6 (br, CH_{arom}/C3), 140.9 (CH_{arom}/C5), 155.7 (N-C_q/C1), 164.0 (ON-C_q/C4). – MS ((+)-FAB): m/z (%) = 732.8 (2) $[M]^+$, 605.0 (79) $[M\text{-}I]^+$, 477.1 (12) $[M\text{-}2I]^+$, 455.0 (100) $[M\text{-}I\text{-}\mathbf{3}]^+$. – $C_{18}H_{25}I_2IrN_2O$ (731.43): calcd. C 29.56, H 3.45, N 3.83; found C 29.74, H 3.47, N 3.79.

*(4-Nitroso-N,N-diethylaniline-N)dichlorido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**6a**)*

Reagents: 165 mg (0.207 mmol) **1a**, 221 mg (1.242 mmol) **4**. Reaction time: 2 h. Yield: 234 mg (0.406 mmol, 98 %) dark-red microcrystalline solid. Brown crystals (blocks) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **6a** in $CHCl_3$. M. p. decomp. > 186 °C. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 269 (6500), 426 (15 400), 512 nm (21 400 L mol^{-1} cm^{-1}). – IR (CH_2Cl_2): ν = 3050 (w), 2981 (m), 2923 (m), 2874 (w), 1600 (vs), 1543 (w), 1531 (m), 1481 (w), 1453 (w), 1418 (w), 1383 (m), 1370 $\nu(N=O)$ (m), 1346 (m), 1334 (m), 1309 (m), 1248 (m), 1190 (w), 1167 (w), 1137 (vs), 1075 (m), 1029 (w), 1010 (w), 878 (w), 827 (m), 629 (w), 608 (w), 592 (w) cm^{-1}. – IR (ATR, solid): ν = 2965 (w), 2914 (w), 2870 (w), 1597 (s), 1532 (m), 1482 (w), 1448 (w), 1416 (w), 1366 $\nu(N=O)$ (w), 1326 (s), 1305 (s), 1246 (s), 1187 (w), 1166 (w), 1127 (vs), 1073 (s), 1029 (s), 1009 (m), 955 (w), 930 (w), 872 (m), 832 (m), 794 (w), 755 (w), 716 (s), 627 (w), 605 (m) cm^{-1}. – ^1H NMR (270.17 MHz, $CDCl_3$): δ = 1.25 (t, 6 H, ^3J = 7.13 Hz, Et-CH_3), 1.51 (s, 15 H, Cp-CH_3), 3.47 (q, 4 H, ^3J = 7.13 Hz, N-CH_2), 6.52 (d, 2 H, ^3J = 9.78 Hz, CH_{arom}/H2+H6), 8.27 (br, 2 H, CH_{arom}/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 8.9 (Cp-CH_3), 12.8 (Et-CH_3), 46.1 (N-CH_2), 88.2 (Cp-C_q), 110.8 (CH_{arom}/C2+C6), 132.6 (br, CH_{arom}/C3+C5), 155.0 (N-C_q/C1), 163.7 (ON-C_q/C4). – MS ((+)-FAB): m/z (%) = 576.0 (2) $[M]^+$, 541.1 (89) $[M\text{-}Cl]^+$, 505.2 (27) $[M\text{-}2Cl]^+$, 363.2 (100) $[M\text{-}Cl\text{-}\mathbf{4}]^+$. – $C_{20}H_{29}Cl_2IrN_2O$ (576.58): calcd. C 41.66, H 5.07, N 4.86; found C 41.48, H 5.03, N 4.58.

*(4-Nitroso-N,N-diethylaniline-N)dibromido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**6b**)*

Reagents: 149 mg (0.153 mmol) **1b**, 164 mg (0.918 mmol) **4**. Reaction time: 4 h. Yield: 180 mg (0.270 mmol, 88 %) dark-green microcrystalline solid. Black crystals (blocks) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **6b** in $CHCl_3$. M. p. decomp. > 188 °C. – IR (CH_2Cl_2): ν = 3049 (w), 2981 (w), 2919 (w), 2879 (w), 1600 (vs), 1540 (w), 1532 (m), 1488 (w), 1455 (w), 1418 (w), 1383 (w), 1369 $\nu(N=O)$ (w), 1346 (m), 1333 (m), 1308 (m), 1246 (m), 1191 (w), 1167 (w), 1135 (vs), 1075 (m), 1029 (w), 1010 (w), 878 (w), 827 (m), 630 (w), 609 (w), 594 (w) cm^{-1}. – IR (ATR, solid): ν = 2976 (w), 2962 (w), 2918 (w), 2868 (w), 1598 (s), 1535 (m), 1487 (w), 1466 (w), 1449 (w), 1417 (m), 1375 (w), 1366 $\nu(N=O)$ (w), 1356 (w), 1338 (w), 1323 (s), 1300 (s), 1249 (s), 1190 (w), 1168 (w), 1131 (vs), 1073 (s), 1027 (m), 1004 (m), 980 (w), 965 (w), 932 (w), 876 (m), 840 (m), 833 (m), 799 (w), 736 (w), 717 (s), 627 (w), 606 (m) cm^{-1}. – ^1H NMR (399.78 MHz, $CDCl_3$): δ = 1.26 (t, 6 H, ^3J = 7.16 Hz, Et-CH_3), 1.58 (s, 15 H, Cp-CH_3), 3.47 (q, 4 H, ^3J = 7.12 Hz, N-CH_2), 6.52 (d, 2 H, ^3J = 9.19 Hz, CH_{arom}/H2+H6), 8.26 (br, 2 H, CH_{arom}/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 9.4 (Cp-CH_3), 12.8 (Et-CH_3), 46.0 (N-CH_2), 89.0 (Cp-C_q), 110.5 (CH_{arom}/C2+C6), 132.5 (br, CH_{arom}/C3+C5), 154.9 (N-C_q/C1), 164.2 (ON-C_q/C4). – MS ((+)-FAB): m/z (%) = 664.9 (6) $[M]^+$, 585.0 (95) $[M\text{-}Br]^+$, 505.2 (38) $[M\text{-}2Br]^+$, 407.1 (100) $[M\text{-}Br\text{-}\mathbf{4}]^+$. – $C_{20}H_{29}Br_2IrN_2O$ (665.48): calcd. C 36.10, H 4.39, N 4.21; found C 36.47, H 4.35, N 4.24.

*(4-Nitroso-N,N-diethylaniline-N)diiodido(pentamethyl-η^5-cyclopentadienyl)iridium(III) (**6c**)*

Reagents: 245 mg (0.211 mmol) 1 c, 226 mg (1.266 mmol) **4**. Reaction time: 7 h. Yield: 281 mg

(0.370 mmol, 88 %) dark-green microcrystalline solid. Black crystals (blocks) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **6c** in CH_2Cl_2. M. p. decomp. > 179 °C. – IR (CH_2Cl_2): ν = 3044 (w), 2980 (w), 2916 (w), 2876 (w), 1600 (vs), 1544 (w), 1525 (m), 1478 (w), 1452 (w), 1416 (w), 1380 $\nu(\mathrm{N=O})$ (m), 1347 (m), 1334 (m), 1307 (m), 1242 (m), 1191 (w), 1166 (w), 1127 (vs), 1076 (m), 1027 (w), 1010 (w), 877 (w), 826 (m), 630 (w), 608 (w), 596 (w) cm^{-1}. – IR (ATR, solid): ν = 2974 (w), 2964 (w), 2927 (w), 2910 (w), 2868 (w), 1592 (s), 1540 (m), 1531 (m), 1484 (w), 1464 (w), 1450 (w), 1416 (m), 1356 $\nu(\mathrm{N=O})$ (w), 1342 (w), 1321 (s), 1297 (s), 1243 (s), 1188 (w), 1167 (w), 1121 (vs), 1069 (s), 1024 (m), 1004 (m), 973 (w), 961 (w), 929 (w), 868 (m), 836 (m), 826 (m), 790 (w), 732 (w), 716 (s), 628 (m), 604 (m) cm^{-1}. – ^{1}H NMR (399.78 MHz, $CDCl_3$): δ = 1.26 (t, 6 H, ^3J = 7.16 Hz, Et-CH_3), 1.73 (s, 6 H, Cp-CH_3), 1.81 (s, 9 H, Cp-CH_3), 3.48 (q, 4 H, ^3J = 7.24 Hz, N-CH_2), 6.58 (br, 2 H, CH_{arom}/H2+H6), 8.28 (br, 2 H, CH_{arom}/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 10.5 (Cp-CH$_3$), 10.9 (Cp-CH$_3$), 12.7 (Et-CH$_3$), 45.6 (N-CH$_2$), 89.0 (Cp-C_q), 90.2 ($C_{\mathrm{q,\,arom}}$), 110.1 (CH$_{\mathrm{arom}}$/C2+C6), 132.9 (br, CH$_{\mathrm{arom}}$/C3+C5), 154.0 (N-C_q/C1), 164.3 (ON-C_q/C4). – MS ((+)-FAB): *m/z* (%) = 760.9 (4) $[M]^+$, 633.0 (100) $[M\text{-}I]^+$, 505.2 (19) $[M\text{-}2I]^+$, 455.0 (98) [M-I-**4**]$^+$. – $C_{20}H_{29}I_2IrN_2O$ (759.48): calcd. C 31.63, H 3.85, N 3.69; found C 32.05, H 3.87, N 3.74.

*Synthesis of the rhodium(III) complexes **7a** and **8a***

The dimer $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**2a**) and six equivalents of ligand **3** or **4** were dissolved in 20 mL of dry dichloromethane and stirred at room temperature. The solvent showed a dark-red color instantly. After the reaction was completed (see time below) the dichloromethane was removed *in vacuo*. For purification 20 mL of dry Et_2O was added, and the mixture was stirred for 30 min at room temperature. Then, the precipitate was separated by centrifugation and Et_2O was removed with a cannula. This procedure was repeated 3 times to remove excess ligand, and the resulting product was dried *in vacuo* for 12 h at 50 °C.

*(4-Nitroso-N,N-dimethylaniline-N)dichlorido(pentamethyl-η^5-cyclopentadienyl)rhodium(III) (**7a**)*

Reagents: 142 mg (0.230 mmol) **2a**, 207 mg (1.380 mmol) **3**. Reaction time: 2 h. Yield: 164 mg (0.357 mmol, 78 %) red microcrystalline solid. Red crystals (platelets) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **7a** in $CHCl_3$. M. p. decomp. > 177 °C. – IR (CH_2Cl_2): ν = 3049 (w), 2978 (w), 2919 (w), 2864 (w), 1604 (vs), 1556 (w), 1530 (m), 1477 (w), 1444 (w), 1418 (w), 1402 (w), 1365 $\nu(\mathrm{N=O})$ (s), 1339 (s), 1310 (m), 1229 (m), 1143 (s), 1123 (vs), 1022 (w), 991 (w), 940 (w), 871(w), 825 (m), 632 (w), 606 (w), 585 (w) cm^{-1}. – IR (ATR, solid): ν = 3040 (w), 2988 (w), 2968 (w), 2911 (w), 2856 (w), 1599 (s), 1551 (w), 1533 (w), 1480 (w), 1440 (w), 1398 (w), 1382 (w), 1364 $\nu(\mathrm{N=O})$ (m), 1336 (vs), 1314 (vs), 1290 (w), 1253 (s), 1225 (w), 1146 (vs), 1082 (w), 1062 (w), 1017 (m), 989 (w), 935 (w), 867 (w), 834 (s), 795 (w), 736 (s), 628 (m), 608 (m) cm^{-1}. – ^{1}H NMR (270.17 MHz, $CDCl_3$): δ = 1.59 (s, 15 H, Cp-CH_3), 3.16 (s, 6 H, N-CH_3), 6.63 (d, 2 H, ^3J = 8.89 Hz, CH_{arom}/H2+H6), 7.91 (br, 2 H, CH_{arom}/H3+H5). – ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 9.5 (Cp-CH$_3$), 40.7 (N-CH$_3$), 94.2 (d, $^1J_{\mathrm{Rh\text{-}C}}$ = 8.3 Hz, Cp-C_q), 110.4 (CH$_{\mathrm{arom}}$/C2+C6), 155.7 (N-C_q/C1), 163.0 (ON-C_q/C4)[1]. – MS ((+)-FAB): *m/z* (%) = 423.1 (73) $[M\text{-}Cl]^+$, 273.1 (100) [M-Cl-**3**]$^+$, 237.2 (61) [M-2Cl-**3**]$^+$. – $C_{18}H_{25}Cl_2N_2ORh$ (459.21): calcd. C 47.08, H 5.49, N 6.10; found C 46.49, H 5.39, N 5.78.

*(4-Nitroso-N,N-diethylaniline-N)dichlorido(pentamethyl-η^5-cyclopentadienyl)rhodium(III) (**8a**)*

Reagents: 138 mg (0.223 mmol) **2a**, 238 mg (1.338 mmol) **4**. Reaction time: 4 h. Yield: 136 mg (0.279 mmol, 63 %) dark-red microcrystalline solid. Green crystals (blocks) were obtained by slow isothermic diffusion of *n*-pentane into a solution of **8a** in $CHCl_3$. M. p. decomp. > 137 °C. – IR (CH_2Cl_2): ν = 3046 (w), 2980 (m), 2917 (w), 2876 (w), 1602 (vs), 1541 (w), 1524 (m), 1478 (w), 1452 (w), 1422 (w), 1377 $\nu(\mathrm{N=O})$ (s), 1348 (s), 1335 (s), 1309 (m), 1240 (m), 1192 (w), 1169 (w), 1143 (s), 1123 (vs), 1076 (m), 1022 (w), 1010 (w), 826 (m), 630 (w), 606 (w) cm^{-1}. – IR (ATR, solid): ν = 3072 (w), 2975 (w), 2966 (w), 2909 (w), 2868 (w), 1598 (s), 1537 (m), 1486 (w), 1468 (w), 1444 (w), 1420 (w), 1366 $\nu(\mathrm{N=O})$ (w), 1341 (m), 1330 (s), 1309 (s), 1252 (s), 1189 (w), 1168 (m), 1136 (vs), 1073 (s), 1021 (m), 1007 (m), 931 (w), 870 (m), 846 (m), 800 (w), 715 (s), 628 (w), 605 (m) cm^{-1}. – ^{1}H NMR (399.78 MHz, $CDCl_3$): δ = 1.26 (t, 6 H, ^3J = 7.16 Hz, Et-CH_3), 1.60 (s, 15 H, Cp-CH_3), 3.50 (q, 4 H, ^3J = 7.12 Hz, N-CH_2), 6.61 (br, 2 H, CH_{arom}/H2+H6), 9.02 (br, 2 H, CH_{arom}/H3+H5). – ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 9.5 (Cp-CH$_3$), 12.8 (Et-CH$_3$), 45.6 (N-CH$_2$), 94.2 (d, $^1J_{\mathrm{Rh\text{-}C}}$ = 8.6 Hz, Cp-C_q), 110.1 (CH$_{\mathrm{arom}}$/C2+C6), 154.0 (N-C_q/C1), 162.7 (ON-C_q/C4)[2]. – MS ((+)-FAB): *m/z* (%) = 451.1 (87) $[M\text{-}Cl]^+$, 273.1 (100) [M-Cl-**4**]$^+$, 237.2 (58) [M-2Cl-**4**]$^+$. – $C_{20}H_{29}Cl_2N_2ORh$ (487.27): calcd. C 49.30, H 6.00, N 5.75; found C 48.83, H 5.86, N 4.65.

Single-crystal structure determinations

Single-crystal X-ray data were collected using a Nonius Kappa CCD diffractometer equipped with a rotating anode

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[1] Signal for C3+C5 (too broad) not detected.

[2] Signal for C3+C5 (too broad) not detected.

generator using graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). All structures were solved by Direct Methods with the SHELXS [61] software and refined by full-matrix least-squares on F^2 with SHELXL-97 [61] using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were calculated in ideal positions as riding atoms (except hydrogen bonds in **6a**) by using isotropic displacement parameters. The structure determination of **8a** was added as proof of the coordination but should not be used for a detailed discussion because the final refinement R values were relatively poor.

CCDC 881822–881828 (see Table 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[1] A. Baeyer, H. Caro, *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 809 – 811.
[2] A. Baeyer, H. Caro, *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 963 – 968.
[3] A. Baeyer, *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 1638 – 1640.
[4] R. H. Pickard, J. Kenyon, *J. Chem. Soc., Trans.* **1907**, *91*, 896 – 905.
[5] B. G. Gowenlock, G. B. Richter-Addo, *Chem. Rev.* **2004**, *104*, 3315 – 3340.
[6] B. G. Gowenlock, G. B. Richter-Addo, *Chem. Soc. Rev.* **2005**, *34*, 797 – 809.
[7] B. G. Gowenlock, G. B. Richter-Addo, *J. Chem. Educ.* **2008**, *85*, 1243 – 1245.
[8] M. Cameron, B. G. Gowenlock, G. Vasapollo, *Chem. Soc. Rev.* **1990**, *19*, 355 – 379.
[9] J. Lee, L. Chen, A. H. West, G. B. Richter-Addo, *Chem. Rev.* **2002**, *102*, 1019 – 1066.
[10] H. Yamamoto, N. Momiyama, *Chem. Commun.* **2005**, 3514 – 3525.
[11] W. Adam, O. Krebs, *Chem. Rev.* **2003**, *103*, 4131 – 4146.
[12] H. Waldmann, *Synthesis* **1994**, *1994*, 535 – 551.
[13] J. Streith, A. Defoin, *Synthesis* **1994**, *1994*, 1107 – 1117.
[14] P. F. Vogt, M. J. Miller, *Tetrahedron* **1998**, *54*, 1317 – 1348.
[15] D. Keilin, E. F. Hartree, *Nature* **1940**, *151*, 390 – 391.
[16] Q. H. Gibson, *Biochem. J.* **1960**, *77*, 519 – 526.
[17] M. Murayama, *J. Biol. Chem.* **1960**, *235*, 1024 – 1028.
[18] J. B. Schenkman, B. J. Wilson, D. L. Cinti, *Biochem. Pharmacol.* **1972**, *21*, 2373 – 2383.
[19] M. R. Franklin, *Mol. Pharmacol.* **1974**, *10*, 975 – 985.
[20] D. Mansuy, P. Beaune, J. C. Chottard, J. F. Bartoli, P. Gans, *Biochem. Pharmacol.* **1976**, *25*, 609 – 612.
[21] D. Mansuy, P. Battioni, J. C. Chottard, M. Lange, *J. Am. Chem. Soc.* **1977**, *99*, 6441 – 6443.
[22] D. Mansuy, P. Beaune, T. Cresteil, C. Bacot, J.-C. Chottard, P. Gans, *Eur. J. Biochem.* **1978**, *86*, 573 – 579.
[23] D. M. Gooden, H. Chakrapani, E. J. Toone, *Curr. Top. Med. Chem.* **2005**, *5*, 687 – 705.
[24] C. J. Popp, R. O. Ragsdale, *Inorg. Chem.* **1968**, *7*, 1845 – 1848.
[25] R. Wilberger, C. Krinninger, H. Piotrowski, P. Mayer, I.-P. Lorenz, *Eur. J. Inorg. Chem.* **2004**, 2488 – 2492.
[26] C. Krinninger, C. Högg, H. Nöth, J. C. G. Ruiz, P. Mayer, O. Burkacky, A. Zumbusch, I.-P. Lorenz, *Chem. Eur. J.* **2005**, *11*, 7228 – 7236.
[27] H. L. M. van Gaal, J. P. J. Verlaan, *J. Organomet. Chem.* **1977**, *133*, 93 – 105.
[28] G. Vasapollo, P. Giannoccaro, C. F. Nobile, F. Allegretta, *J. Organomet. Chem.* **1984**, *270*, 109 – 114.
[29] G. Vasapollo, C. F. Nobile, P. Giannoccaro, F. Allegretta, *J. Organomet. Chem.* **1984**, *277*, 417 – 422.
[30] G. Vasapollo, A. Sacco, C. F. Nobile, M. A. Pellinghelli, M. Lanfranchi, *J. Organomet. Chem.* **1988**, *353*, 119 – 123.
[31] G. Vasapollo, C. F. Nobile, A. Sacco, B. G. Gowenlock, L. Sabbatini, C. Malitesta, P. G. Zambonin, *J. Organomet. Chem.* **1989**, *378*, 239 – 244.
[32] G.-e. Matsubayashi, T. Tanaka, *J. Chem. Soc., Dalton Trans.* **1990**, 437 – 441.
[33] M. Cameron, B. G. Gowenlock, G. Vasapollo, *Polyhedron* **1994**, *13*, 1371 – 1377.
[34] R. Rella, P. Siciliano, A. Tepore, L. Valli, G. Vasapollo, *Mater. Sci. Forum* **1996**, *203*, 155 – 160.
[35] R. Rella, A. Serra, G. Vasapollo, L. Valli, *Thin Solid Films* **1996**, *284 – 285*, 69 – 72.
[36] S. Wirth, F. Barth, I.-P. Lorenz, *Dalton Trans.* **2012**, *41*, 2176 – 2186.
[37] P. R. Sharp, D. W. Hoard, C. L. Barnes, *J. Am. Chem. Soc.* **1990**, *112*, 2024 – 2026.
[38] D. W. Hoard, P. R. Sharp, *Inorg. Chem.* **1993**, *32*, 612 – 620.
[39] T. Iwasa, H. Shimada, A. Takami, H. Matsuzaka, Y. Ishii, M. Hidai, *Inorg. Chem.* **1999**, *38*, 2851 – 2859.
[40] M. Cameron, B. G. Gowenlock, R. V. Parish, G. Vasapollo, *J. Organomet. Chem.* **1994**, *465*, 161 – 166.
[41] B. G. Gowenlock, M. J. Maidment, K. G. Orrell, I. Prokes, J. R. Roberts, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1904 – 1911.

[42] B. M. Al-Tahou, B. G. Gowenlock, *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 353 – 355.

[43] B. G. Gowenlock, M. Cameron, A. S. F. Boyd, B. M. Al-Tahou, P. McKenna, *Can. J. Chem.* **1994**, *72*, 514 – 518.

[44] D. A. Fletcher, B. G. Gowenlock, K. G. Orrell, V. Šik, *Magn. Reson. Chem.* **1995**, *33*, 561 – 569.

[45] M. Cameron, B. G. Gowenlock, G. Vasapollo, *J. Organomet. Chem.* **1989**, *378*, 493 – 496.

[46] H. J. Talberg, *Acta Chem. Scand.* **1977**, *31a*, 743 – 751.

[47] B. G. Gowenlock, K. G. Orrell, V. Sik, G. Vasapollo, *Polyhedron* **1998**, *17*, 3495 – 3500.

[48] C. Rømming, H. J. Talberg, *Acta. Chem. Scand.* **1973**, *27*, 2246 – 2248.

[49] M. R. Churchill, S. A. Julis, *Inorg. Chem.* **1977**, *16*, 1488 – 1494.

[50] M. R. Churchill, S. A. Julis, *Inorg. Chem.* **1979**, *18*, 1215 – 1221.

[51] M. R. Churchill, S. A. Julis, F. J. Rotella, *Inorg. Chem.* **1977**, *16*, 1137 – 1141.

[52] N. Escola, A. Llebaría, G. Leitus, F. Doctorovich, *Organometallics* **2006**, *25*, 3799 – 3801.

[53] M.-T. Youinou, R. Ziessel, *J. Organomet. Chem.* **1989**, *363*, 197 – 208.

[54] D. M. Tellers, R. G. Bergman, *Organometallics* **2001**, *20*, 4819 – 4832.

[55] S. Greulich, A. Klein, A. Knodler, W. Kaim, *Organometallics* **2002**, *21*, 765 – 769.

[56] P. Govindaswamy, Y. A. Mozharivskyj, M. R. Kollipara, *Polyhedron* **2005**, *24*, 1710 – 1716.

[57] D. F. Kennedy, B. A. Messerle, M. K. Smith, *Eur. J. Inorg. Chem.* **2007**, *2007*, 80 – 89.

[58] R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.* **1990**, *29*, 2023 – 2025.

[59] D. S. Gill, P. M. Maitlis, *J. Organomet. Chem.* **1975**, *87*, 359 – 364.

[60] J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, *91*, 5970 – 5977.

[61] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473; *ibid.* **2008**, *A64*, 112 – 122.