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Inorganica Chimica Acta 291 (1999) 438–447

Inorganica Chimica Acta

Comparing structures and reactivity in analogous Fe and Ru complexes. (^{i}Pr-DAB)Fe(CO)$_2$I$_2$ and (^{i}Pr-DAB)FeI$_2$: a perfectly reversible CO-carrier system. (R-DAB = N,N'-R$_2$-1,4-diaza-1,3-butadiene)

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Received 25 March 1999

Abstract

Fe(^{i}Pr-DAB)(CO)$_3$ (**1a**) oxidatively adds I$_2$ to give (^{i}Pr-DAB)Fe(CO)$_2$-*trans*-I$_2$ (**2a**). Photochemically or thermally, **2a** readily dissociates both carbonyl ligands to give tetrahedral Fe(^{i}Pr-DAB)I$_2$ (**3a**). Under an atmosphere of CO, complex **2a** is quantitatively regenerated from **3a**. The X-ray crystal structures of **2a** and **3a** have been determined. **2a**: triclinic, space group $P\bar{1}$, $a = 8.7624(3)$, $b = 9.0550(4)$, $c = 10.6512(6)$ Å, $\alpha = 95.429(4)$, $\beta = 105.245(4)$, $\gamma = 95.209(3)°$, $Z = 2$, $R = 0.0251$. **3a**: orthorhombic, space group $Aba2$, $a = 11.2693(10)$, $b = 15.933(2)$, $c = 7.5958(10)$ Å, $Z = 4$, $R = 0.036$. Contrasting the behaviour of **2a**, the analogous ruthenium complexes (R-DAB)Ru(CO)$_2$*trans*-I$_2$ (**4**) are very stable, and the carbonyl ligands cannot be dissociated thermally. In the dichloro complexes, of which both the kinetic *trans*- (**5**) and the thermodynamic *cis*-compounds (**6**) have been isolated, both isomers undergo a photochemical CO mono-substitution to give for example the isolable *trans*-dichloro methanol complex (**7**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Iron complexes; Ruthenium complexes; Diazadiene complexes; Carbonyl complexes

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1. Introduction

It is well known that Fe(CO)$_5$ is a stable compound while Ru(CO)$_5$ is not because it spontaneously looses CO to give the stable Ru$_3$(CO)$_{12}$. Likewise, the zerovalent iron complexes (R-DAB)Fe(CO)$_3$ (**1**) are isolable [2–6], while the ruthenium counterparts (R-DAB) Ru(CO)$_3$ are not, because as with Ru(CO)$_5$, they can only be generated and handled in solution under an atmosphere of CO [7]. In this paper we demonstrate that these relative stabilities of the metal–CO bonds are reversed in the oxidation state +2. In order to compare their structures and reactivities, we have prepared some analogous complexes of iron(II) and ruthenium(II) of the composition (R-DAB)M(CO)$_2$Hal$_2$.

The most important and probably most general access towards iron complexes of the type L$_2$Fe(CO)$_2$Hal$_2$, is by reaction of dihalogeno tetracarbonyliron, Fe(CO)$_4$Hal$_2$ [8], with two mono- or a bidentate donor ligand [8–15]. A one-pot synthesis by reacting FeCl$_2$ with the ligand under a CO atmosphere has also been described [16–18]. The chloride can then be exchanged by metathesis with KBr or KI [18]. As opposed to these reactions where the iron is already in

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PII: S0020-1693(99)00162-0

the final oxidation state +2, there are only very few examples where the halogen is oxidatively added to an iron(0) complex $L_2Fe(CO)_3$. Two examples are the syntheses of $(PMe_2Ph)_2Fe(CO)_2I_2$ [18] and (diars)Fe$(CO)_2Hal_2$ [19] (diars = o-$(Me_2As)_2C_6H_4$; Hal = Br, I).

Complexes of the type $L_2Ru(CO)_2Hal_2$ are most conveniently prepared by reacting the polymeric $[L_2Ru(CO)_2Hal_2]_x$ [20–24] with appropriate ligands L [23,25–30]. If the desired complex is not accessible via this method it may be useful to first use labile ligands, e.g. methanol or acetonitrile as coordinating solvents, to break down the polymer, and then displace the coordinated solvent molecules in a consecutive step by the desired ligand. This method has been employed in the present work (with methanol) and by tom Dieck et al. [31]. The interest in complexes with a $Ru(CO)_2Hal_2$-fragment has concentrated on the synthesis of complete sets of all stereoisomers [25,32], their isomerization reactions [33], analysis of their CO stretching vibrations [34–36], and their catalytic properties [37–39]. In the present work, the respective ruthenium complexes were made and used to compare their properties with those of their homologous iron counterparts.

2. Experimental

2.1. General information

Reactions were performed under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. Solvents were carefully dried and distilled under nitrogen. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The mass spectra in FD mode (Varian MAT 311 A, 5 kV emitter, MeOH or THF as solvents) were used with great advantage to control the composition in particular the ruthenium compounds. The dominant natural isotopes of chlorine (**2**), iron (**4**), and ruthenium (**7**) gave rise to great numbers of isotopomers such that the molecular peak often stretches ten or more mass units. Its pattern is characteristic of the sort of elements and number of atoms present. The calculated [40] and observed patterns were found to agree very well in the reported compounds. Photolyses were carried out in a Pyrex immersion well apparatus using a Philips HPK 125 high-pressure mercury lamp.

2.1.1. Starting materials

The diazadiene ligands [41] and the complexes (R-DAB)$Fe(CO)_3$ (**1**) [4–6] have been prepared by known procedures. The diazadiene ligands $R^1{-}N{=}CR^2{-}CR^2{=}N{-}R^1$ employed in this investigation are **a** (R^1=$CH(CH_3)_2$, R^2 = H), **b** (R^1=$C(CH_3)_3$, R^2 = H), **c** (R^1=*cyclo*-C_6H_{11}, R^2 = H), and **d** (R^1=*p*-$OCH_3{-}C_6H_4$, $R^2 = CH_3$).

2.1.1.1. Synthesis of $[Ru(CO)_2Cl_2]_n$. In a modified procedure of Colton and Farthing [23], the polymeric $[Ru(CO)_2Cl_2]_n$ is prepared by dissolving 10.52 g $RuCl_3{\cdot}nH_2O$ in a mixture of 60 ml formic acid and 60 ml concentrated hydrochloric acid. The solution is heated at 120°C for 15 h. Then the clear yellow solution is evaporated to dryness and the residue dried to constant weight in vacuo (ca. 10^{-3} mbar) at 150°C. A total of 6.87 g of $[Ru(CO)_2Cl_2]_n$ was obtained as a yellow powder. IR (MeOH) ν_{CO} = 2066 (s), 1993 (s) cm^{-1}.

2.1.1.2. Synthesis of $[Ru(CO)_2I_2]_n$. After addition of some hypophosphorous acid, hydroiodic acid (ca. 57%) is first distilled. Then 1.09 g $RuCl_3{\cdot}nH_2O$ is suspended in 15 ml of the hydroiodic acid and in vacuo evaporated to dryness three successive times. The resulting black crystalline rutheniumtriiodide is dissolved in a mixture of 20 ml formic acid and 20 ml of the hydroiodic acid and heated at 130°C for 1.5 h. The dark red solution is evaporated to dryness and the residue is dried to constant weight in vacuo (ca. 10^{-3} mbar) at 100°C, yielding 1.45 g of $[Ru(CO)_2I_2]_n$ (3.53 mmol Ru) as an orange powder. IR (MeOH) ν_{CO} = 2120 (m), 2055 (s) cm^{-1}.

2.2. Formation of complexes (R-DAB)$Fe(CO)_2I_2$ (**2**)

2.2.1. (^{i}Pr-DAB)$Fe(CO)_2I_2$ (**2a**)

To a stirred solution of 1.60 g (5.70 mmol) (^{i}Pr-DAB)$Fe(CO)_3$ (**1a**) in 80 ml of THF was slowly added at 0°C 1 equiv. of I_2 (1.45 g, 5.69 mmol) in 20 ml of THF. After 45 min the solvent was removed by evaporation. After crystallization from toluene/hexane (1:1) under an atmosphere of CO, the product was obtained as violet–black crystals in a yield of 78%. *Anal.* of **2a**: Found: C, 23.62; H, 3.26; N, 5.48, Fe, 11.18. Calc.: C, 23.74; H, 3.19; N, 5.54; Fe 11.04%. IR (toluene) ν_{CO}: 2040 (s), 2000 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 80 MHz) ppm: 8.59 (s, 2H, =C*H*–N), 5.32 (sp, 2H, N–C*H*$(CH_3)_2$, $^3J_{H,H}$ 6.4 Hz), 1.82 (d, 12H, $^3J_{H,H}$ 6.4 Hz).

2.2.2. (pAn-DAB; Me,Me)$Fe(CO)_2I_2$ (**2d**)

Analogous to the preparation of **2a** from 0.40 g (0.92 mmol) (pTol-DAB)$Fe(CO)_3$ (**1d**) in 30 ml THF, and 0.23 g (0.91 mmol) I_2 in 10 ml THF. Yield (recrystallized twice from toluene/hexanes) 0.28 g (0.42 mmol, 46%) of black crystals of **2d**. *Anal.* of **2d**: Found: C, 36.25; H, 3.10; N, 4.27; I, 38.40. Calc.: C, 36.28; H, 3.05; N, 4.23; I, 38.34%. IR (toluene) ν_{CO}: 2047 (s), 2010 (s) cm^{-1}. MS (FD): $m/e = 662$ (M^+).

2.3. Formation of complex (^{i}Pr-DAB)FeI$_2$ (**3a**)

2.3.1. Photochemically

A solution of 740 mg (1.46 mmol) **2a** in 100 ml of toluene was irradiated for 15 min. After removal of the solvent by evaporation, the crude product was crystallized from a concentrated solution in toluene/hexane to give 510 mg (78%) of complex **3a** as black crystals. Complex **2a** can be completely regenerated by stirring a toluene solution of **3a** under an atmosphere of CO.

2.3.2. Thermally

A solution of 280 mg (0.55 mmol) **2a** in 20 ml toluene was stirred at 40–45°C for 7 h. The reaction proceeds with evolution of CO and can be monitored by IR. The intensely green solution is cooled to room temperature (r.t.), and inversely filtered off the black precipitate, which is washed with toluene. The combined toluene solutions are concentrated in vacuo and cooled at −20°C to give another crop of black crystals. Total yield of **3a**: 0.20 g (80%). *Anal.* of **3a**: Found: C, 21.33; H, 3.63; N, 6.18; I, 56.50. Calc.: C, 21.36; H, 3.58; N, 6.23; I, 56.42%. MS (FD): $m/e = 900$ (4%, dimer [(^{i}Pr-DAB)FeI$_2$]$_2^+$), 450 (100%, [(^{i}Pr-DAB)FeI$_2$]$^+$).

2.4. X-ray data collection, solution and refinement of the structures of complexes **2a** and **3a**[3]

X-ray data were collected on an Enraf–Nonius CAD4T (Rotating Anode) diffractometer at 150 K for red (**2a**) and yellow–brown (**3a**) cut-to-size inert oil covered crystals. Numerical details have been collected in Table 1. Structures were solved by Patterson techniques (DIRDIF [42]) (**2a**) or Direct Methods SHELXS 86 [43]) (**3a**) and refined on F^2 with SHELXL96 [44] (**2a**) and SHELXL93 [45] (**3a**). Correction for absorption was done with a modified DIFABS [46] for **3a** and analytically [47] for **2a**. Hydrogen atoms were included at calculated positions and refined riding on their carrier atoms. A BASF/TWIN parameter [0.0(3)] was refined to establish the absolute structure of **3a**. Geometry calculation and the ORTEP illustrations were done with PLATON [48].

2.5. Formation of complexes (R-DAB)Ru(CO)$_2$(trans-Hal)$_2$

2.5.1. Formation of (^{i}Pr-DAB)Ru(CO)$_2$(trans-I)$_2$ (**4a**)[4]

In total 0.64 g (1.6 mmol) $1/n$[Ru(CO)$_2$I$_2$]$_n$ and 0.22 g (1.6 mmol) ^{i}Pr-DAB were dissolved in 40 ml THF, and stirred in the dark for 1 day at r.t. The solvent was removed in vacuo and the brown residue recrystallized twice from acetone to give 0.20 g (0.36 mmol, 23%) of dark orange crystals of **4a**. *Anal.* of **4a**: Found: C, 22.30; H, 3.01; N, 5.08. Calc.: C, 21.79; H, 2.93; N, 5.08%. IR (MeOH) ν_{CO}: 2052 (s), 1998 (m) cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): 8.53 (d, 2H, $^4J_{H,H}$ 0.8 Hz, =C*H*–N), 4.60 (dsp, 2H, $^3J_{H,H}$ 6.5 Hz, $^4J_{H,H}$ 0.8 Hz, C*H*(CH$_3$)$_2$), 1.63 (d, 12H, $^3J_{H,H}$ 6.5 Hz, C*H*$_3$).

2.5.2. Thermal stability of **4a**

In total 50 mg of **4a** were dissolved in 0.6 ml of acetone-d$_6$. The red–orange solution was heated in a sealed NMR tube in an oven at 180°C for 14 h. The subsequently measured ^{1}H NMR spectrum showed in addition to the bulk of unchanged **4a** only two signals of very low intensity at 8.07 ppm (s, =C*H*–N) and 1.51 ppm (d, C*H*$_3$) which have to be assigned to free ^{i}Pr-DAB, probably from beginning thermal decomposition. There is no indication of a formation of the *cis*-diiodo complex.

Table 1
Crystal data and details of the structure determinations

Compound	**2a**	**3a**
Crystal data		
Empirical formula	$C_{10}H_{16}FeI_2N_2O_2$	$C_8H_{16}FeI_2N_2$
Formula weight	505.90	449.88
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$ (no. 2)	*Aba*2 (no. 41)
a (Å)	8.7624(3)	11.2693(10)
b (Å)	9.0550(4)	15.933(2)
c (Å)	10.6512(6)	7.5958(10)
α (°)	95.429(4)	
β (°)	105.245(4)	
γ (°)	95.209(3)	
V (Å^3)	805.80(7)	1363.9(3)
Z	2	4
D_{calc} (g cm^{-3})	2.085	2.191
F(000)	476	840
μ(Mo Kα) (mm^{-1})	4.8	5.6
Crystal size (mm)	$0.13 \times 0.25 \times 0.25$	$0.10 \times 0.13 \times 0.25$
Data collection		
Temperature (K)	150	150
Radiation Mo Kα (Å)	0.71073	0.71073
θ min., max. (°)	2.0, 27.5	2.6, 25.0
Dataset	−11:11; −11:11; −13:13	−13:13; 0:18; −9:0
Total data	7680	1261
Unique data	3679	652
R_{int}	0.080	0.059
Observed data [$I > 2.0\sigma(I)$]	3040	494
Refinement		
N_{ref}, N_{par}	3679, 166	652, 63
R, wR, S	0.0251, 0.0455, 1.06	0.0362, 0.0677, 0.98
Max., average shift/error	0.00, 0.00	0.00, 0.00
Min., max. residual density (e Å^{-3})	−0.94, 0.83	−0.64, 0.66

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[3] Full details may be obtained from the author A.L. Spek.

[4] **4a** had at the same time been described by tom Dieck et al. [31].

Table 2
Preparation and characterization of compounds (R-DAB)$Ru(CO)_2$(*trans*-$Cl)_2$ (**5a**–**d**)

Compound	$(^{i}$Pr-DAB) $Ru(CO)_2Cl_2$ (**5a**)	(tBu-DAB) $Ru(CO)_2Cl_2$ (**5b**)	(cHex-DAB) $Ru(CO)_2Cl_2$ (**5c**)	(pAn-DAB;Me,Me) $Ru(CO)_2Cl_2$ (**5d**)
Starting materials				
$[Ru(CO)_2Cl_2]_n$ (g, mmol Ru)	0.45, 1.97	0.94, 4.12	1.31, 5.75	0.66, 2.89
R-DAB **a**–**d** (g, mmol)	0.26, 1.85	0.69, 4.10	1.26, 5.72	0.85, 2.87
Reaction time (h)	48	18	24	1 (reflux)
Appearance	big orange crystals	light yellow crystals	dark yellow needles	light yellow crystals
Yield (gl, mmol %)	0.11; 0.3; 16	0.24; 0.61; 15	0.57; 1.27; 22	0.38; 0.72; 25
FD-MS: M^+ (*m/e*)	362–373	391–401	442–551	
IR(MeOH) ν_{CO} (cm^{-1})	2063 (s), 2003 (m)	2061 (s), 1999 (m)	2061 (s), 2002 (m)	
IR (KBr pellet), ν_{Ru-Cl} (cm^{-1})	325		335	
Formula	$C_{10}H_{16}Cl_2N_2O_2Ru$	$C_{12}H_{20}Cl_2N_2O_2Ru$	$C_{16}H_{24}Cl_2N_2O_2Ru$	$C_{20}H_{20}Cl_2N_2O_4Ru$
M_w	368.23	396.28	448.36	524.37
Anal. % Found (Calc.)				
C	32.70 (32.62)	36.42 (36.37)	42.78 (42.86)	44.88 (45.81)
H	4.44 (4.38)	5.10 (5.09)	5.38 (5.40)	3.89 (3.84)
N	7.58 (7.61)	7.12 (7.07)	6.21 (6.25)	5.45 (5.34)
O	8.86 (8.07)	8.31 (8.07)	7.09 (7.14)	12.13 (12.20)
Cl	19.33 (19.26)	17.86 (17.89)		
^1H NMR, δ (ppm) (mult), acetone-d_6, 300 K, **5a**–**c**: 80 MHz **5d**: 300 MHz	CH=N 8.62 (d) $^4J_{H,H}$ 0.8 Hz $CH(CH_3)_2$ 4.49 (dsp) $^3J_{H,H}$ 6.5 Hz, $^4J_{H,H}$ 0.8 Hz $CH(CH_3)_2$ 1.55 (d) $^3J_{H,H}$ 6.5 Hz	CH=N 8.61 (s) CH_3 1.64 (s)	CH=N 8.58 (d) $^4J_{H,H}$ 1.0 Hz =N–CH 3.92–7.34 (m) CH_2 (ring) 1.10–2.35	N=C–CH_3 2.58 (s) CH (Ph 2,3) 7.04–7.34 (m), O–CH_3 3.88 (s)
^{13}C NMR, δ (ppm), acetone-d_6, 300 K, **5a**–**c**: 20 MHz **5d**: 75 MHz	CO 197.47 CH=N 164.14 $^1J_{C,H}$ 180.7 Hz $CH(CH_3)_2$ 65.97 $^1J_{C,H}$ 141.1 Hz $CH(CH_3)_2$ 23.06 $^1J_{C,H}$ 128.0 Hz	CO 197.83, CH=N 163.60 $C(CH_3)_3$ 67.68 $C(CH_3)_3$ 30.29	CO 197.76, CH=N 164.13, cHex–CH(1) 73.74 cHex-CH_2(2) 34.11 cHex-CH_2(3) 25.72 cHex-CH_2(4) 26.00	CO 196.47 CH=N 177.37 $C(CH_3)$=N 20.71, $^1J_{C,H}$ 130.6 Hz, CPh(1) 143.55, CH Ph(2) 123.00, $^1J_{C,H}$ 164.5 Hz, $^2J_{C,H}$ 6.1 Hz, CHPh(3) 115.36, $^1J_{C,H}$ 162.9 Hz $^2J_{C,H}$ 5.0 Hz CPh(4) 160.13 O–CH_3 55.90

*2.5.3. General procedure for the formation of (R-DAB)Ru(CO)$_2$(trans-Cl)$_2$ (**5**)*

Polymeric $[Ru(CO)_2Cl_2]_n$ is stirred in methanol at r.t. until a clear light yellow solution is obtained. After addition of the diazadienes **a**–**d** the mixture is stirred in the dark for the times specified in Table 2. The solvent is consecutively removed in vacuo and the residue is recrystallized twice from methanol.

*2.6. Experiments towards the formation of complexes all-cis-(R-DAB)Ru(CO)$_2$Cl$_2$ (**6**)*

*2.6.1. All-cis-(^{i}Pr-DAB)Ru(CO)$_2$Cl$_2$ (**6a**)*

In solution: 0.44 g (1.19 mmol) **5a** was dissolved in 20 ml acetonitrile and refluxed in the dark. The isomerization reaction can be monitored by IR or NMR, and is finished after 5 h. The residue, after removal of the solvent in vacuo, was recrystallized from methanol yielding 0.28 g (0.76 mmol, 64%) of light yellow crystals of **6a**.

In the solid state: an orange crystal (10 mg) of **5a** was heated in an oil bath at 140°C for 3 h giving a light yellow crystalline powder, which by IR and ^1H NMR was identified as pure **6a**.

MS (FD): $m/e = 367–373$ ($m/e = M^+$). *Anal.* of **6a**: Found: C, 32.71; H, 4.34; N, 7.62; O, 8.83; Cl, 19.33. Calc.: C, 32.62; H, 4.38; N, 7.61; O, 8.69; Cl, 19.26%. IR (MeOH) ν_{CO}: 2068 (s), 2007 (s) cm^{-1}. ^1H NMR (300 K, 80 MHz, acetone-d_6, ppm): 8.66, 8.57 (2 × d, broad, CH–N), 4.94 (dsp, $^3J_{H,H}$ 6.6 Hz, $^4J_{H,H}$ 1.2 Hz, $CH(CH_3)_2$), 4.29 (dsp, $^3J_{H,H}$ 6.5 Hz, $^4J_{H,H}$ 0.8 Hz, $CH'(CH_3)_2$), 1.51 (2 × d, 6H, $^3J_{H,H}$ 6.6 Hz, CH_3), 1.45 (2 × d, 6H, $^3J_{H,H}$ 6.5 Hz, CH_3). ^{13}C NMR (300 K, 75 MHz, acetone-d_6, ppm): 196.97, 189.87 (CO), 165.99 (=CH–N; $^1J_{C,H}$ 120.9 Hz, $^nJ_{C,H}$ 13.0, 6.3 Hz), 164.40 (=C'H–N; $^1J_{C,H}$ 122.5 Hz, $^nJ_{C,H}$ 13.0, 6.9 Hz), 67.69 ($CH(CH_3)_2$; $^1J_{C,H}$ 145.6 Hz), 59.05 ($C'H(CH_3)_2$; $^1J_{C,H}$ 146.4 Hz), 23.26, 23.13 ($CH(CH_3)_2$; $^1J_{C,H}$ 127.7 Hz), 23.09, 22.33 ($CH(C'H_3)_2$; $^1J_{C,H}$ 145.6 Hz).

2.6.2. Equilibrium between (tBu-DAB)(CO)$_2$Ru(trans-Cl)$_2$ (**5b**) and (tBu-DAB)(CO)$_2$Ru(cis-Cl)$_2$ (**6b**)

A total of 50 mg of **5b** were dissolved in 0.6 ml acetone-d$_6$, and the light yellow solution was heated in an oven at 130°C in a sealed NMR tube. The isomerization reaction was monitored by ^{1}H NMR. After 18 h a stable equilibrium composition between **5b** and **6b** of 43:57 was reached. The solvent was evaporated and the light yellow residue was twice recrystallized from methanol, giving 10 mg of light yellow crystals, which were identified by ^{1}H NMR as a 30:70 mixture of **5b** and **6b**. This sample was again heated at 130°C upon which (now from the other side) a stable equilibrium composition between **5b** and **6b** again of 43:57 was reached. ^{1}H NMR of **6b** (300 K, 80 MHz, acetone-d$_6$, ppm): 8.57, 8.51 (2 × d, =C*H*–N, $^3J_{H,H}$ 1.2 Hz), 1.70, 1,57 (2 × s, C*H*$_3$).

2.6.3. Equilibrium between (cHex-DAB)(CO)$_2$Ru(trans-Cl)$_2$ and (cHex-DAB)(CO)$_2$(cis-Cl)$_2$ (**5c** and **6c**)

A total of 50 mg of **5c** were dissolved in 0.6 ml acetone-d$_6$ and the light yellow solution was heated in an oven at 130°C in a sealed NMR tube. After 10 h, the reaction had apparently gone to completion, showing only the signals of **6c**. On cooling the sample to r.t., most of **6c** crystallized in pure form and was isolated. In the supernatant mother liquor, however, both **5c** and **6c** were still present in a ratio of 13:87 as was indicated by ^{1}H NMR. ^{1}H NMR of **6c** (300 K, 80 MHz, acetone-d$_6$, ppm): 8.59, 8.53 (2 × 1H, s, broad, =C*H*–N), 4.57, 3.97 (2 × 1H, s, broad, N–C*H*), 1.4–2.3 (m, 20H, ring-C*H*$_2$).

2.7. Photochemical substitution of CO in cis- and trans-(R-DAB)Ru(CO)$_2$Cl$_2$

2.7.1. Photolysis of (^{i}Pr-DAB)Ru(CO)$_2$(trans-Cl)$_2$ (**5a**)

On irradiation of the light yellow solution of 0.44 g (1.19 mmol) **5a** in 80 ml methanol, CO is evolved and the colour changes to deep red. The reaction was monitored by IR and had gone to completion after 20 min. The solvent was removed in vacuo at r.t. leaving a quantitative yield of almost black crystals of (^{i}Pr-DAB)Ru(CO)(MeOH)(*trans*-Cl)$_2$ (**7a**). The product was spectroscopically pure and no further purification was necessary. *Anal.* for **7a**: Found: C, 32.24; H, 5.46; N, 7.58; O, 8.60; Cl, 18.97. Calc.: C, 32.27; H, 5.42; N, 7.53; O, 8.60; Cl, 19.05%. MS (FD): $m/e = 677$–682 [(^{i}Pr-DAB)Ru(CO)(Cl)$_2$]$_2^+$. The isotopic pattern of the molecular ion could not be observed, only that of the dimer after loss of methanol. IR (MeOH) ν_{CO}: 1967 cm^{-1}, (THF) ν_{CO}: 1955 cm^{-1}. ^{1}H NMR (300 K, 300 MHz, methanol-d$_4$) ppm: 8.56, 8.11 (2 × s broad, 1H, =C*H*–N), 4.61 (dsp, 1H, $^3J_{H,H}$ 6.6 Hz, $^4J_{H,H}$ 1.2 Hz, C*H*(CH$_3$)$_2$), 4.34 (dsp, 1H, $^3J_{H,H}$ 6.6 Hz, $^4J_{H,H}$ 0.9 Hz, C*H'*(CH$_3$)$_2$), 1.50, 1.38 (2 × d, 6H, $^3J_{H,H}$ 6.6 Hz, CH(C*H*$_3$)$_2$), 4.82 (s, 1H, O*H*), 3.29 (s, 3H, OC*H*$_3$). ^{13}C NMR (300 K, 20 MHz, methanol-d$_4$) ppm: 203.74 (*C*O), 162.94, 160.07 (=*C*H–N), 23.25, 23.01 (CH–(*C*H$_3$)$_2$).

2.7.2. Photolysis of (^{i}Pr-DAB)Ru(CO)$_2$(cis-Cl)$_2$ (**6a**)

Irradiation of a solution of 0.29 g (0.79 mmol) **6a** in 100 ml of methanol for 45 min and evaporation of the solvent yielded 0.29 g (0.79 mmol) red–black crystals of **7a**, identical with the product starting from **5a**.

Stability of **7a**: from solutions of **7a** in methanol at r.t. after several hours a light red precipitate of polymeric **8a** [(^{i}Pr-DAB)Ru(CO)(Cl)$_2$]$_n$ is formed (*Anal.* of **8a**: Found: C, 31.63; H, 4.73; N, 7.82. Calc. C, 31.77; H, 4.74; N, 8.24%, which on refluxing completely redissolves under formation of **7a**. **8a** is also formed when **7a** is dissolved in THF or acetone, or when **7a** is irradiated in THF or benzene.

2.7.3. Photolysis of (pAn-DAB;Me,Me)Ru(CO)$_2$(trans-Cl)$_2$ (**5d**)

Photolysis of 20 mg **5d** in 8 ml of methanol in a Pyrex cuvette was monitored by IR and proceeded to completion after 45 min. After evaporation of the solvent, a quantitative yield of red–black crystals of (pAn-DAB;Me,Me)Ru(CO)(MeOH)(*trans*-Cl)$_2$ (**7d**) was obtained. IR (methanol) ν_{CO}: 1976 cm^{-1}. ^{1}H NMR (300 K, 300 MHz, methanol-d$_4$) ppm: 7.22, 7.00 (2 × m, 4H, phenyl-*H*), 4.86 (s, 1H, CH$_3$O*H*), 3.85, 3.84 (2 × s, 3H, Ph–OC*H*$_3$), 3.34 (s, 3H, C*H*$_3$OH), 2.57, 2.40 (s, 3H, =C(C*H*$_3$)–N). ^{13}C NMR (300 K, 75 MHz, methanol-d$_4$) ppm: 201.44 (*C*O), 177.33, 173.94 (=*C*(Me)–N), 160.44, 160.08 (phenyl, *p*-), 148.57, 140.86 (phenyl, *ipso*), 125.03, 122.62 (phenyl, *o*-), 115.32, 114.97 (phenyl, *m*-), 55.99 (O*C*H$_3$), 21.10, 20.70 (*C*H$_3$).

Stability of **7d**: clear red solutions of **7d** in various solvents are stable. No formation of polymeric [(pAn-DAB;Me,Me)Ru(CO)(*trans*-Cl)$_2$]$_n$ analogous to **8a** is observed.

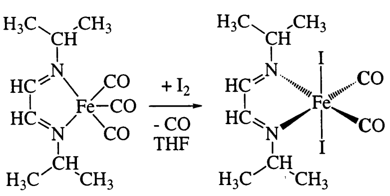
2.8. Displacement of the coordinated methanol in **7a** and **7d** by CO

When solutions of **7a** and **7d** in methanol are stirred in an autoclave, under 70–80 bar of CO pressure at r.t. for several hours, the coordinated methanol is cleanly replaced by CO under formation of **5a** and **5d** which have been identified by IR and ^{1}H NMR.

3. Results

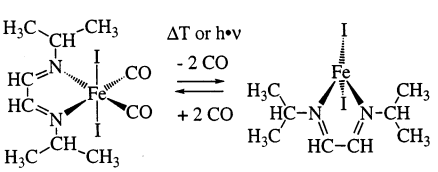
*3.1. Complexes (R-DAB)Fe(CO)$_2$I$_2$ (**2**) and (R-DAB)FeI$_2$ (**3**)*

Diazadiene-tricarbonyl-iron complexes (**1a**,**b**,**d**) react in solution with iodine, already at low temperatures, with liberation of CO to stereoselectively give diazadiene-dicarbonyl-*trans*-diiodo-iron(II) (**2**) (Eq. (1)).



1a **2a** (1)

The dark violet complexes **2** are very labile and very readily react further, both thermally and photochemically, to give under CO-loss tetrahedral high spin complexes **3**. This reaction is perfectly reversible in the case of **2a** and **3a** (Eq. (2)). When, e.g. the green toluene solution of **3a** is stirred under an atmosphere of CO at r.t., the deep violet **2a** is quantitatively reformed.



2a **3a** (2)

In the ^{1}H NMR spectrum of **2a**, there is a single set of resonances for the protons of both halves of the ^{i}Pr-DAB ligand and there is no diastereotopic splitting of the doublet of the isopropyl methyl groups. Due to the high quadrupole moment of the two iodo ligands (nuclear spin 5/2), the resonance lines are clearly broader than those in the starting tricarbonyl complex **1a**. However, the hyperfine splitting of the isopropyl resonances is clearly visible, and the coupling constants are readily determined. This is not the case in the ^{1}H NMR spectrum of **3a**, which only shows broad humps without much fine structure at ca. 7.7 ppm (imine H), 4.6 ppm (methyne H), and a very broad doublet at 1.5 ppm (methyl). The FD mass spectrum of **3a** shows two peaks, a small one at $m/e = 900$ of 4% relative intensity, corresponding to a dimeric structure, [^{i}Pr-DAB)FeI$_2$]$_2^+$, and a base peak (100% rel. int.) at $m/e = 450$ (M^+). From this it was not clear whether the strong line broadening in the NMR had to be ascribed to four bridging iodines in a closed-shell dimeric structure with an 18e configuration on both of the iron atoms, or to the paramagnetism in a mononuclear complex with a 14e high-spin configuration. Therefore, an X-ray structure determination was undertaken.

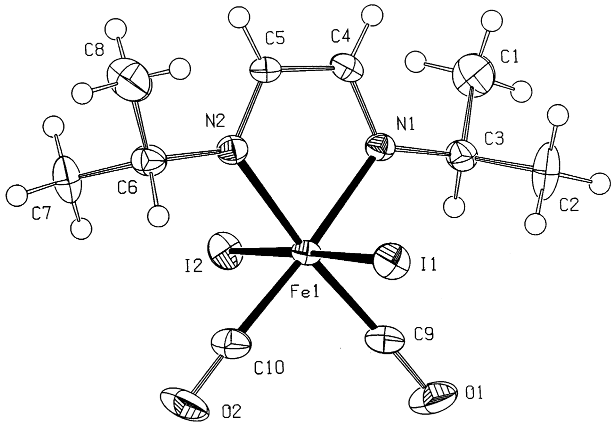


Fig. 1. Crystal structure of **2a**. The thermal ellipsoids are drawn at the 50% probability level.

When the oxidative addition of iodine is done with **1b** (R^1 = tert-butyl), the carbonyl ligands are further labilized in **2b**, which is therefore only observable by IR as a short-lived intermediate, and the only isolable product is **3b**. This may be due to the greater steric bulk of the tert-butyl groups.

*3.1.1. Molecular structures of **2a** and **3a***

The crystal structures of complexes **2a** and **3a** are shown in Figs. 1 and 2, together with the atomic numbering. Tables 3 and 4 give selected bond lengths and angles. **2a** crystallizes with two molecules in a general position in a triclinic unit cell and **3a** with four molecules (each located on a crystallographic two-fold axes) in an orthorhombic unit cell. The structure of **3a** is non-centrosymmetric and polar. In **2a** iron is coordinated octahedrally with two *trans*-positioned I, two *cis*-positioned C=O and two *cis*-coordinated N of the ^{i}Pr-DAB moiety. In **3a** iron is coordinated tetrahedrally with two I and two N of the ^{i}Pr-DAB moiety. Bond distances (Tables 2 and 3) in the ^{i}Pr-DAB moiety are

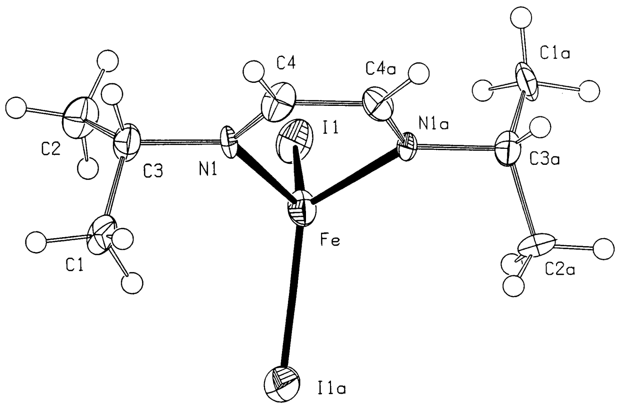


Fig. 2. Crystal structure of **3a**. The thermal ellipsoids are drawn at the 50% probability level.

Table 3
Selected bond distances (Å) and angles (°) for **2a**

Bond distances (Å)			
Fe1–I1	2.6173(4)	C4–C5	1.437(5)
Fe1–I2	2.6147(4)	C9–O1	1.130(5)
Fe1–N1	1.975(3)	C10–O2	1.138(5)
Fe1–N2	1.980(3)		
Fe1–C10	1.793(4)		
N2–C5	1.283(5)		
Fe1–C9	1.787(4)		
N1–C4	1.285(5)		
Bond angles (°)			
I1–Fe1–I2	177.64(2)		
N1–Fe1–N2	80.81(12)		
C9–Fe1–C10	88.58(18)		

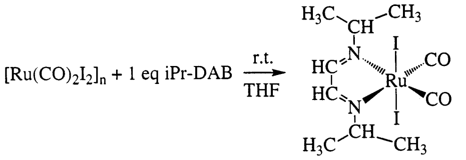
essentially the same for **2a** and **3a**. The major difference involves the conformation of the ^{i}Pr groups. The Fe–I distances observed in **2a** (2.6173(4) and 2.6147(4) Å) are significantly longer than those found for **3a** (2.576(2) Å).

A search in the Cambridge Crystallographic Database [49] for other structures containing the $FeNeI_2$ fragment gave only one hit for a structure containing the tetrahedral dinitrosyl-diiodo-iron species [50] with Fe–I distances 2.584 and 2.596 Å.

3.2. Ruthenium complexes

3.2.1. Complexes (R-DAB)Ru(CO)$_2$Hal$_2$

Complexes **4**–**7** (cf. Eq. (2) and Scheme 1) have been prepared in moderate yields in order to compare their chemical properties with those of **2a**. When the direct homologue of **2a**, i.e. the *trans*-diiodo ruthenium complex **4a** had been prepared, tom Dieck et al. [31] reported on a series of such compounds, and only the dichloro complexes were further investigated. The published X-ray data of (pTol-DAB)Ru(CO)$_2$-*trans*-I$_2$ [31] are used to compare its structural features with those of **2a** (vide infra).

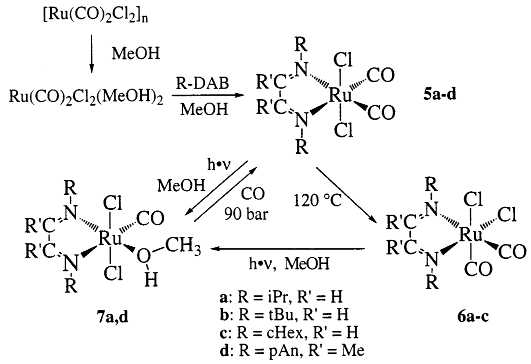


4a

(3)

Table 4
Selected bond distances (Å) and angles (°) for **3a**

Bond distances (Å)	
Fe–I1	2.576(2)
Fe–N1	2.123(14)
N1–C4	1.23(2)
N1–C3	1.501(16)
C4–C4a	1.467(18)
Bond angles (°)	
I1–Fe–I1a	110.96(12)
N1–Fe–N1a	76.5(5)



Scheme 1.

The reaction of polymeric [Ru(CO)$_2$Cl$_2$]$_n$ with diazabutadienes **a**–**d** in strongly coordinating solvents such as methanol or acetonitrile leads, in a kinetically controlled reaction, stereoselectively to the formation of the *trans*-dichloro complexes **5a**–**d**. No other conformational isomers can be detected. When a less strongly coordinating solvent such as THF was used, a complex mixture of isomers was obtained, which have not further been analyzed. Contrasting the stability of **4a**, which cannot thermally be isomerized even under drastic conditions (180°C for 14 h), complexes **5a**–**d** isomerize on warming in solution or in the solid state to the racemic all-*cis* isomers **6**, which are readily identified from their NMR spectra. The two equivalent halves of the R-DAB ligands in **5** become inequivalent in **6**, giving rise to two sets of resonances. In addition, due to the C_1 symmetry of **6** with the chiral ruthenium centre, the methyl groups of the *N*-^{i}Pr groups in **6a** are diastereotopically split. The temperatures at which the isomerizations take place is characteristic for each compound and seems to depend on the steric properties of the R-DAB ligand. While **5a** is stable in refluxing methanol, it isomerizes smoothly and quantitatively to **6a** at ca. 80°C in refluxing acetonitrile. In the solid state a higher temperature of ca. 140°C is required. Complex **5b** (R = tBu) isomerizes in solution at 130°C to give an equilibrium mixture containing **5b** and **6b** in a ratio of 43:57 (determined by NMR); this equilibrium composition can be established from both sides. Complex **5c** (R = cHex) isomerizes at 120°C to give **6c** with a very low residual concentration of **5c**.

3.2.2. Formation and reactivity of complexes (R-DAB) Ru(CO)(MeOH)(trans-Cl)$_2$ (7)

Photochemically, one of the two CO ligands in **5** and **6** can be dissociated in solution. Even in diffuse daylight, dilute solutions of **5** and **6** are slowly photolyzed. Photolysis with a high-pressure mercury lamp in methanol or THF solution is complete within a few minutes. With vigorous evolution of CO, the light yellow solutions become dark red. The resulting methanol complexes **7a**,**d**, which are formed from either **5** (*trans*-Cl_2) or **6** (*cis*-Cl_2), are isolable, and have the chloro ligands in *trans*-configuration and the coordinated methanol in the plane of the R-DAB ligand (cf. Scheme 1). The THF complex is too labile to be isolable; on evaporation of the solvent, an inhomogeneous almost insoluble red solid is obtained. When a methanol solution of **7a** is left standing for several hours, again a light red solid **8a** precipitates, which can be completely redissolved in boiling methanol regenerating **7a**. The red solids appear to be solvent-free polymeric $[(\text{R-DAB})\text{Ru(CO)}\textit{trans}\text{-Cl}_2]_n$. Contrasting the lability of the methanol ligand in **7a**, methanol solutions of **7d** appear indefinitely stable, but at r.t. under a CO pressure of 90 bar, in both **7a** and **7d**, the methanol ligand is cleanly substituted for CO, giving complexes **5a**,**d**.

4. Discussion

4.1. Configuration and reactivity of complexes (R-DAB)M(CO)$_2$Hal$_2$

The formation of complexes **2** by oxidative addition of iodine to the tricarbonyl complexes **1** (Eq. (1)) can be readily monitored by IR spectroscopy. The oxidation of Fe(0) to Fe(II) results in a pronounced shift of the carbonyl stretching bands toward higher frequencies by about 70 and 30 cm^{-1}. The resulting two CO bands (A_1 and B_2) are of almost identical intensity, indicating OC–Fe–CO angles close to 90°, i.e. relative *cis*-positions. In an all-*cis* configured octahedral complex (C_1 symmetry), the two halves of the R-DAB ligand would be inequivalent, having a carbonyl and an iodine in *trans*-positions of the two nitrogens. The NMR spectra of **2**, however, show only one set of resonances for the R-DAB ligands. Therefore, complexes **2** must have C_{2V} symmetry with *trans*-configured iodines, which is confirmed by the X-ray structural analysis of **2a** (see below).

Regardless of the halogen and the diazadiene ligand, all ruthenium complexes **4** and **5a**–**d** show two carbonyl stretching bands of comparable intensity; in the low frequency region, only one strong absorption is found and assigned to the Ru–Cl stretching vibration (**5a**: 325 cm^{-1}; **5c**: 335 cm^{-1}). A single set of NMR resonances is observed for the R-DAB ligands, and diastereotopic splitting for the N–^{i}Pr methyl groups is absent. This again indicates C_{2V} symmetry with *trans*-configured iodines, and agrees with the spectroscopic properties of known examples of this structural type [30,31,36].

The most striking difference in reactivity between **2a** and its direct homologue **4**, or the analogous chloro complexes **5a**–**d**, concerns the stability of the M–CO bonds. Thermally, the Ru–CO bond in **4** and **5a**–**d** cannot be broken. A solution of **4** was heated in an evacuated sealed NMR tube at 180°C for 14 h, and in addition to the bulk of unchanged **4**, only very minor amounts of free ^{i}Pr-DAB, indicating beginning disruption of the complex, could be observed. In complexes **5**, only one of the two CO ligands can be photochemically dissociated (cf. Sections 2.7 and 3.2.2). In contrast, both carbonyl ligands in **2a** readily dissociate photochemically and also thermally slightly above r.t. (Eq. (2)) to give quantitative yields of the 14e-complex **3a**. In solution, **2a** and **3a** are in a perfectly reversible equilibrium which can be shifted back and forth for any number of times. Under 1 atm of CO pressure, the equilibrium lies completely on the side of **2a** at r.t. Qualitative experiments indicated that the equilibrium position depends on the CO partial pressure.

When solutions of the *trans*-dichloro complexes **5a**–**c** are heated in the dark, they isomerize to the obviously thermodynamically more stable all-*cis* complexes **6a**–**c**. The *trans*-diiodo complex **4** does not isomerize even at 180°C (see above). This does not necessarily mean that in this case this is the thermodynamically most stable configuration, but the reason could also be that the bulky iodines impose too high an activation barrier. The isomerization of **5a**–**c** proceeds in methanol, acetone, or acetonitrile solutions at normal pressure or in a sealed tube, and also in the solid state, i.e. there is no influence of the reaction medium. During the isomerization reaction there are no colour changes, and, with IR or NMR monitoring, no intermediates can be observed. The reaction is very clean, i.e. there are no side reactions such as CO substitution or formation of dimers. This is indicative of an intramolecular process. The intramolecular isomerization of octahedral complexes has been intensively studied [51], and the most likely process here is a Bailar–twist [52] through a trigonal prismatic transition state. The observed dependence of the isomerization temperatures on the bulk of the nitrogen substituents in the R-DAB ligands (^{i}Pr < cHex < tBu) is in agreement with such a process. The only alternative that has to be considered is intermediate dechelation $\kappa^2 \rightarrow \kappa^1$ of the diazadiene ligand, with consecutive Berry pseudorotation in the resulting five-coordinate species, and rechelation. The fluxionality of cationic (R-DAB)(allyl)Pd(II) complexes has been explained by such a dechelation–rechelation of the R-DAB ligand [53–55], but we believe this is less likely in the present case.

4.2. Comparison of the crystal and molecular structures of **2a**, **3a**, and (pTol-DAB;Me,Me)Ru(CO)$_2$I$_2$ (**4e**)

We expected that the enormous difference in the stability of the M–CO bond in the two homologous Fe and Ru complexes **2a** and **4a** would be clearly reflected

Table 5
Bond lengths (Å) in the N=C–C=N backbone of R-DAB ligands

Compound	**2a**	**3a**	Free **c** [56]
N=C	1.285(5)	1.23(2)	1.258(3)
C–C	1.437(5)	1.467(18)	1.457(3)

in the metal-to-carbon and/or carbon-to-oxygen bond lengths. The structure of **4a** has not been determined because that of (pTol-DAB;Me,Me)Ru(CO)$_2$I$_2$ (**4e**) had already been published by tom Dieck et al. [31]. The bond lengths from the central metal to the coordinated N, C, and I atoms in **2a** and **4e** are all approximately 0.1 Å shorter for iron than for ruthenium, which reflects the different radii of the two metals. So the Fe–C9 (1.787(4) Å) and Fe–C10 (1.793(4) Å) bonds are not exceptionally long and the C–O bonds of the carbonyl ligands in **2a** and **4e** (**2a**: C9–O1 1.130(5) Å, C10–O2 1.138(5) Å; **4e**: C–O 1.139(7) Å) are almost identical. They show absolutely no indication of a different amount of π-backdonation into the C≡O π*-orbitals, which might explain the different M–CO bond strengths.

The structure determination of **4e** had the additional bonus that the complex molecules **4e** cocrystallized with one molecule of free, uncoordinated R-DAB ligand in the lattice. This gave the additional information that there is almost no π-backdonation from the Ru to the R-DAB ligand, because the C=N (1.28 Å) and the central C–C (1.50 Å) bond lengths of the free and coordinated R-DAB ligand are identical within experimental error [31].

Because the electronic and steric properties of the isopropyl and cyclohexyl substituents are practically identical, the bond lengths within the N=C–C=N backbone of the ^{i}Pr-DAB ligand in **2a** and **3a** can be compared with those of the free cHex-DAB structure which has been determined by Keijsper et al. [56] (Table 5).

The differences are small but instructive. In **2a**, the N=C distance is greater and the C–C distance is smaller than in free **c**. In **3a**, on the other hand, the N=C distance is somewhat smaller than in free **c**, while the C–C distances are the same within experimental error. This means that in the 18e-complex **2a**, the R-DAB LUMO, which is N=C antibonding and C–C bonding, still gets some electron density from the metal via π-backdonation, while in the 14e-complex **3a** the R-DAB ligand acts as a pure σ-donor.

5. Conclusions

A perfectly reversible CO-carrier system has been discovered, based on (^{i}Pr-DAB)FeI$_2$ (**3a**) a stable monomeric 14e-configured Fe(II) complex. In solution under an atmosphere of CO, **3a** quantitatively takes up two molecules of CO to form the isolable complex **2a** which in turn thermally, already slightly above r.t., or photochemically, looses both carbonyl ligands to re-form **3a**. Complexes **4** and **5**, ruthenium analogues of **2**, have been prepared and their thermal and photochemical reactivity has been investigated. Contrasting the behaviour of **2**, the carbonyl ligands in the *trans*-diiodo complexes **4** and *trans*-dichloro complexes **5** are very strongly bound and cannot be thermally dissociated. The dichloro complexes **5** thermally only isomerize to the thermodynamically more stable all-*cis* complexes **6**. Photochemically, only one of the two carbonyl ligands can be exchanged for a molecule of donor solvent, THF or methanol. The X-ray molecular structures of the analogous *trans*-diiodo iron and ruthenium complexes **3** and **4** do not reflect, and do not provide any information on the vastly different stability of their M–CO bonds.

Acknowledgements

This work was supported in part by the Fonds der Chemischen Industrie, and by the Council for Chemical Research of the Netherlands, Organisation for Scientific Research (CW-NWO).

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