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Synthesis and structure of 1,2,4-triazol-2-ium-5-ylidene complexes of Hg(II), Pd(II), Ni(II), Ni(0), Rh(I) and Ir(I)

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Abstract

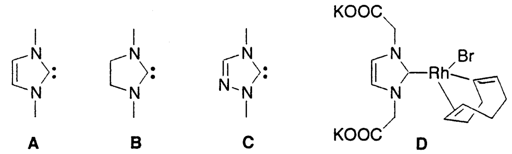
The reaction of $M(OAc)_2$ [M = Hg(II), Pd(II), Ni(II)] or $M(acac)(CO)_2$ [M = Rh(I), Ir(I)] with dicationic 1,2,4-triazolium salts **2** affords a series of water-soluble 1,2,4-triazol-2-ium-5-ylidene complexes **4**–**8**, arising from deprotonation-complexation of the N-heterocyclic ligand. Reduction of $[Ni(trz)_2I_2(TfO)_2]$ (trz = 1,2,4-triazol-2-ium-5-ylidene) (**6a**) with zinc powder in the presence of carbon monoxide results in the formation of the corresponding Ni(0)–carbene complexe **9**. The latter has also been prepared by the reaction of $Ni(CO)_4$ with the corresponding in situ generated triazoliumylidene. The solid state structure of $[Hg(trz)_2(dmso)(TfO)_4]$ (**4**), $[Pd(trz)_2I_4]$ (**5a**), $[Ni(trz)_2I_2(TfO)_2]$ (**6a**) and $[Ni(trz)_2(CO)_2]$ (**9**) were determined by single-crystal X-ray diffraction studies.

Keywords: Synthesis; 1,2,4-Triazol-2-ium-5-ylidene complexes; N-Heterocyclic carbene ligand

1. Introduction

Since the development of the Ruhrchemie-Rhone Poulenc 'oxo' process in which the two basic problems of homogenous catalysis—separation and recycling of the catalyst—have been elegantly resolved by using a water-soluble rhodium complex, the concept of two-phase homogenous catalysis continues to be a strong motivation for the elaboration of new hydrophilic ligands and their metal complexes [1]. In recent years interest has grown in performing reactions such as hydroformylation [2], C/C-coupling [3], olefin metathesis [4] and many other industrially important transformations under biphasic conditions in which the catalyst is dissolved only in one phase. Not surprisingly, much of the focus of this work has been on functionalized phosphine ligands carrying polar or ionic moieties, such as sulfonate, carboxylate, ammonium, phosphonium and hydroxyl groups [5].

Recently, N-heterocyclic carbenes (NHC) **A**–**C** (Scheme 1), so called 'phosphine mimics', have shown to be very promising candidates for constructing a variety of novel transition metal complexes with potential application in homogenous catalysis [6–8]. These ligands are strong σ-donors, and in this regard, they resemble tertiary alkylphosphines. However, in contrast to phosphines the carbene ligands do not readily undergo dissociation from the metal centre, even at elevated temperatures, and form metal complexes that have remarkable stability towards heat, oxygen and moisture [9]. Very limited efforts have been made, to develop rational synthetic routes to hydrophilic amino-



Scheme 1.

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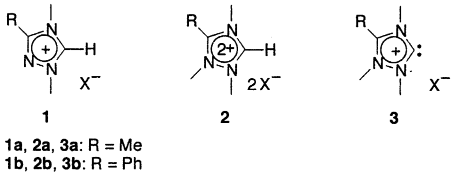
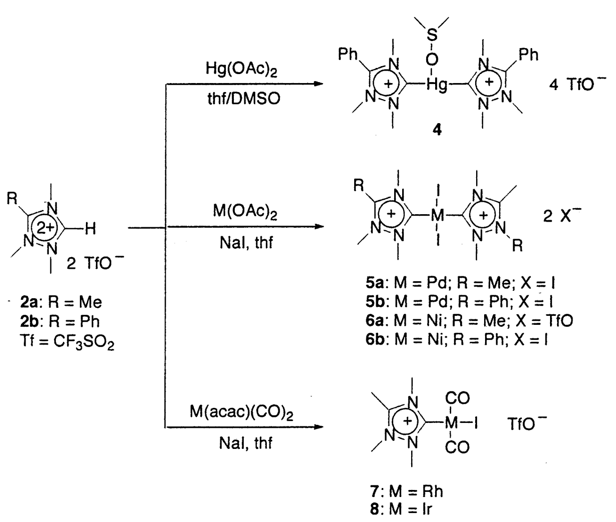
carbene ligands. The first water-soluble imidazolydene–rhodium complex **D** featuring carboxylate groups on side chains has recently been synthesized by Herrmann et al. [10], but preparation of suitably functionalized aminocarbene complexes remains a challenge in synthetic coordination chemistry. In this context, it was of interest to investigate the possibility of synthesizing metal complexes bearing charged azolydene units that might both stabilize the metal in low oxidation states and confer hydrophilic properties to the complex. Here, we report the synthesis and structural characterization of the first water-soluble 1,2,4-triazol-2-ium-5-ylidene complexes of Hg(II), Pd (II), Ni(II), Ni(0), Rh(I) and Ir(I).

2. Results and discussion

The obvious precursors for the desired 1,2,4-triazol-2-ium-5-ylidenes **3** are dicationic triazolium salts **2**, which in turn can be synthesized by alkylation of 1,2,4-triazolium salts **1** (Scheme 2) [11]. Treatment of derivatives **1** (R = Me, Ph) in dichloromethane with excess CF_3SO_3Me affords **2** in high yields. The presence of a very acidic CH proton in **2** is confirmed by a peak at low field ($\delta_H = 10.7$) in the ^1H-NMR spectra. However, attempted deprotonation of **2** lead to a complex mixture of products, which indicates the high instability of the free triazoliumylidenes **3**. Therefore, for the preparation of metal complexes bearing 1,2,4-triazol-2-ium-5-ylidenes **3** as ligands we used the Wanzlick–Öfele method based on in situ deprotonation of triazolium salts by the appropriate metallic precursor with basic ligands [6–8]. The reaction of compound **2b** with $Hg(OAc)_2$ in THF–DMSO (20:1) leads to complex **4**, which was isolated in 86% yield (Scheme 3). Both ^1H- and ^{13}C-NMR spectra support the complexation of the mercury atom with two triazol-2-ium-5-ylidene moieties and one molecule of DMSO. In the ^{13}C-NMR spectrum the ligating carbon atom is observed at 183.3 ppm with a large coupling constant ($^1J_{C-Hg} = 3275$ Hz), which is characteristic for azolylidene–mercury complexes [12–14]. Single crystals of **4** suitable for an X-ray diffraction study were grown from a methanol–ether solution at room temperature. The solid-state structure is shown in Fig. 1. The mercury atom is in a trigonal-planar environment. The C(1)–Hg–C(12) angle in **4** is reduced to 167.8° compared to the somewhat larger angle in the previously reported bis(imidazolydene)mercury bis(perchlorate) complex (180°) [15], but is larger than in the corresponding dichloride complex (161.4°) [13] in which there are additional interactions between the mercury centre and associated chloride ions. The C(1)N(1)C(2)N(3)N(2) and C(12)N(4)C(13)N(6)N(5) triazolium rings are planar (maximum deviation 0.0021 and 0.0069 Å, respectively) and are twisted against the trigonal-planar coordination sphere of the mercury (60 and 51°, respectively). The Hg–C(1) and Hg–C(12) distances (2.074 and 2.078 Å, respectively) are comparable to those reported for other mercury carbene complexes.



Scheme 2.



Scheme 3.

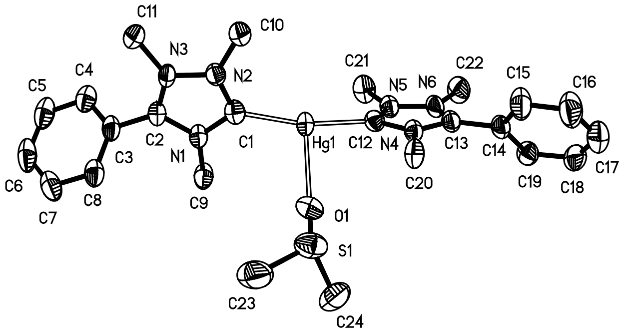


Fig. 1. Molecular structure of **4** in the crystal. Selected bond lengths (Å): Hg(1)–C(1) 2.074(5); Hg(1)–C(12) 2.078(5); Hg(1)–O(1) 2.524(8); C(1)–N(1) 1.366(7); C(1)–N(2) 1.327(7); N(1)–C(2) 1.366(7); C(2)–N(3) 1.313(7); N(2)–N(3) 1.370(6); C(12)–N(5) 1.320(7); C(12)–N(4) 1.363(7); N(4)–C(13) 1.365(7); C(13)–N(6) 1.295(8); N(5)–N(6) 1.366(6); N(1)–C(9) 1.459(7); N(2)–C(10) 1.453(7); N(3)–C(11) 1.472(7); N(4)–C(20) 1.452(7); N(5)–C(21) 1.467(8); N(6)–C(22) 1.477(7). Selected bond angles (°): C(1)–Hg(1)–C(12) 167.8(2); C(1)–Hg(1)–O(1) 97.5(3); C(12)–Hg(1)–O(1) 94.4(3); N(1)–C(1)–N(2) 106.0(5); N(2)–C(1)–Hg(1) 126.1(4); N(1)–C(1)–Hg(1) 127.5(4); N(5)–C(12)–N(4) 106.1(5); N(5)–C(12)–Hg(1) 125.6(4); N(4)–C(12)–Hg(1) 128.2(4).

Deprotonation of **2** with palladium diacetate and nickel diacetate in the presence of NaI (two equivalents) afforded complexes **5** and **6**, which were isolated as dark red solids in good yields. Note that iodide anions are absolutely necessary as stabilizing co-ligands. As expected, complexes **5** and **6** are ionic and hence only slightly soluble in common organic solvents, but soluble in DMSO, methanol and water. Slow diffusion of ether into an acetonitrile solution of **5a** and into an acetone solution of **6a** afforded single crystals suitable for X-ray diffraction studies. Figs. 2 and 3 show the molecular structure of these complexes. In both complexes the metal is in an essentially square planar environment. The triazoliumylidene ligands in **5a** and **6a** adopt a *trans* orientation, probably due to the sterically demanding nature of the permethylated triazolium rings. In related Ni and Pd azolylidene complexes both *cis* and *trans* arrangements have been reported depending on both the steric and electronic character of the carbene ligands [10,14a,16]. Although the cationic triazoliumylidene ligands are evidently more electron-withdrawing in comparison with other N-heterocyclic carbene ligands, the Pd–C (2.017 Å) and Ni–C (1.868 Å) distances in **5a** and **6a** are within the range of typical metal–carbon single bonds. The differences between the ring parameters and C–M bond lengths in **5a** and **6a** follow the general rule that metal–carbon bonds become stronger when going from 3d to 4d transition metals [17]. It should also be noted that the ^{1}H-NMR for **5** and **6** shows two sets of signals for the methyl groups. Most likely due to the unsymmetrical pattern and steric bulk of the triazoliumylidene ligands, complexes **5** and **6** exist in solution as a mixture of two rotamers. Rotamers have already been observed with other bis(carbene) complexes, when the carbene ligands are not symmetrical and are arranged either *cis* or *trans* around palladium [18].

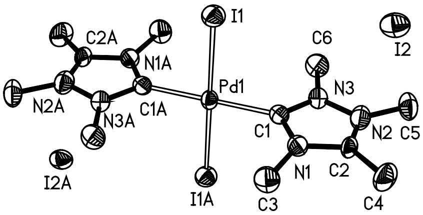


Fig. 2. Molecular structure of **5a**. Selected bond lengths (Å): Pd(1)–C(1) 2.017(5); Pd(1)–C(1A) 2.017(5); Pd(1)–I(1) 2.5941(4); Pd(1)–I(1A) 2.5941(4); C(1)–N(3) 1.345(6); C(1)–N(1) 1.347(6); N(1)–C(2) 1.369(6); N(1)–C(3) 1.465(7); C(2)–N(2) 1.298(7); C(2)–C(4) 1.471(6); N(2)–N(3) 1.371(6); N(2)–C(5) 1.477(7); N(3)–C(6) 1.466(6); C(7)–C(8) 1.435(10); C(8)–N(4) 1.129(9). Selected bond angles (°): C(1)–Pd(1)–C(1A) 180.0; C(1)–Pd(1)–I(1A) 89.25(12); C(1A)–Pd(1)–I(1A) 90.75(12); N(1)–C(1)–N(3) 104.4(4); N(3)–C(1)–Pd(1) 128.6(3); N(1)–C(1)–Pd(1) 127.0(3); C(1)–N(1)–C(2) 110.3(4);N(1)–C(2)–N(2) 107.5(4); C(2)–N(2)–N(3) 107.8(4); C(1)–N(3)–N(2) 110.1(4).

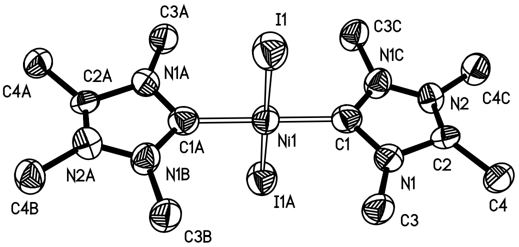


Fig. 3. Molecular structure of **6a**. Selected bond lengths (Å): Ni(1)–C(1) 1.765(3); Ni(1)–C(7) 1.954(2); Ni(1)–C(13) 1.765(3); Ni(1)–C(14) 1.776(3); C(1)–N(1) 1.358(3); C(1)–N(3) 1.361(3); N(1)–C(2) 1.361(3); C(2)–N(2) 1.308(3); N(2)–N(3) 1.366(3); C(7)–N(6) 1.361(3); C(7)–N(4) 1.367(3); N(4)–C(8) 1.365(3); C(8)–N(5) 1.305(3); N(5)–N(6) 1.373(3); C(13)–O(1) 1.150(3); C(14)–O(2) 1.153(3). Selected bond angles (°): C(1)–N(1)–C(2) 111.96(18); C(13)–Ni–C(14) 108.17(13); C(13)–Ni(1)–C(7) 106.65(11); C(14)–Ni(1)–C(7) 114.20(11); C(13)–Ni(1)–C(1) 113.02(10); C(14)–Ni(1)–C(1) 105.57(11); N(1)–C(1)–N(3) 101.96(19); N(6)–C(7)–N(4) 101.8(2).

Reaction of the triazolium salt **2a** with M(acac)$_2$(CO)$_2$ (M = Rh, Ir) in the presence of NaI affords the corresponding carbene–iridium(I) and –rhodium(I) complexes **7** and **8**. The carbene carbon signal appears as a doublet at δ 188 ($^1J_{\mathrm{RhC}} = 42$ Hz) for **7**, and as a singlet at δ 169 for **8**. The two CO-ligands are equivalent as demonstrated by the presence of only one doublet at δ 183 ($^1J_{\mathrm{RhC}} = 83$ Hz) for **7** and one singlet at δ 184 for **8**; this is confirmed by IR spectroscopy [ν (CO): 1975 (**7**); 1974 cm^{-1} (**8**)]. Note, that the L(CO)$_2$RhI (L = *N*,*N*-dimethylimidazolydene) complex has been previously isolated in the *cis* form [19].

Zero-valent metal–NHC complexes, particularly Ni(0)-carbene derivatives, are especially interesting due to their enhanced catalytic activity in Heck and related coupling reactions [17]. Up to now the synthesis of these compounds were based on Ni(0)-precursors, such as Ni(CO)$_4$ or Ni(PPh$_3$)$_4$ [20]. To evaluate the possibility of the preparative reduction of the easily available Ni(II)–carbene complexes **6** into the corresponding Ni(0) derivatives, a voltammetric study of **6a** was performed. Excess of 1,5-cyclooctadiene (COD) was used to stabilize the intermediate electron-rich species that could be formed during the redox process. The cyclic voltamogram of **6a** is shown in Fig. 4. The non-reversible wave at −710 mV is attributed to the reduction of the

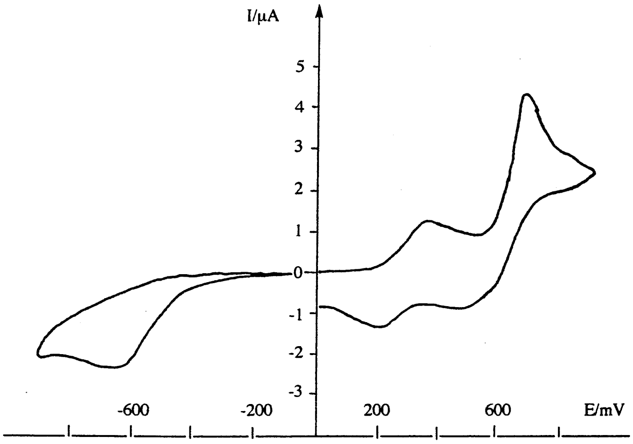
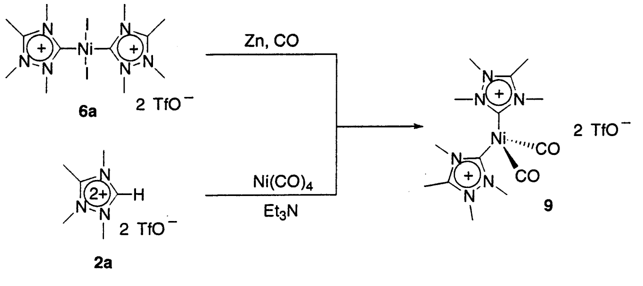


Fig. 4. Cyclic voltamogram of **6a**.

Scheme 4.

complex and the formation of a 14-electron zero-valent species [$L_2Ni(0)$] and two iodide ions (I^-) (Scheme 4). This step should be reversible but the [$L_2Ni(0)$] complex can react with COD to give an 18-electron complex [$L_2Ni(COD)$]. The second wave is observed at 307 mV and is due to the reversible redox reaction of I_2/I^- [21]. The last wave at 642 mV is reversible and might be attributable to the reduction and oxidation of the complex [$L_2Ni(COD)$], which was previously formed. In order to confirm these observations, we performed a reductive electrolysis of **6a** at constant potential. The overall electrical charge necessary for the transformation corresponds to the involvement of two electrons, which is in perfect agreement with the reduction of the complex **6a** into a zero-valent species. We then carried out a voltametric study to control the disappearance of the starting material: the complex **6a** was not present, while the two reversible waves corresponding to I_2/I^- and $[L_2Ni(COD)_2]^{2+}/[L_2Ni(COD)]$ were observed at the same potentials. These results clearly show that the chemical reduction of **6a** should allow the synthesis of a zero-valent complex. In accordance with this conclusion, complex **6a** easily reacts with zinc powder in the presence of carbon monoxide in acetonitrile to give the Ni(0)–carbene complex **9**. The latter has also been prepared by the reaction of $Ni(CO)_4$ with the corresponding triazoliumylidene, in situ generated from **2a**, and triethylamine (Scheme 5). In the ^{1}H- and ^{13}C-NMR spectra for **9**, four signals are observed for the methyl groups suggesting that the two triazoliumylidene ligands are magnetically equivalent. The signal for the carbene carbons appear at low field (δ 200) and are slightly deshielded compared to complex **6a**. The carbonyl ligands are characterized by an IR band at 1982 and 1906 cm^{-1}. Single crystals of **9** suitable for an X-ray diffraction study were obtained at room temperature from an acetonitrile–ether solution. A view of the solid-state structure of **9** is depicted in Fig. 5. The nickel atom has a tetrahedral coordination with a C(1)–Ni(1)–C(7) angle of 109.3(2)°. The Ni–C_{carb} distances of 1.954(2) and 1.956(2) Å are comparatively longer than those observed in the related Ni(II)–carbene complex **6a** (1.868 Å); the endocyclic NCN angles for **6a** and **9** are comparable (Figs. 3 and 4).



Scheme 5.

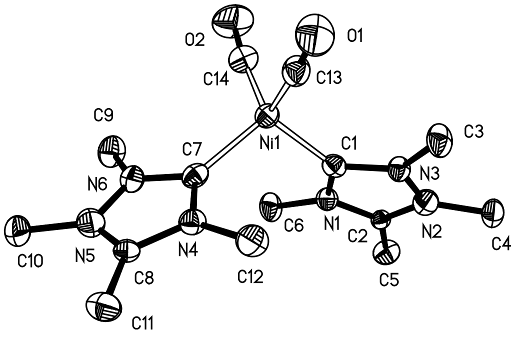


Fig. 5. Molecular structure of **9**. Selected bond lengths (Å): Ni(1)–C(1) 1.956(2); Ni(1)–C(7) 1.954(2); Ni(1)–C(13) 1.765(3); Ni(1)–C(14) 1.776(3); C(1)–N(1) 1.358(3); C(1)–N(3) 1.361(3); N(1)–C(2) 1.361(3); N(1)–C(6) 1.463(3); C(2)–N(2) 1.308(3); C(2)–C(5) 1.461(3); N(2)–N(3) 1.366(3); N(2)–C(4) 1.464(3); N(3)–C(3) 1.456(3); C(7)–N(6) 1.361(3); C(7)–N(4) 1.367(3); N(4)–C(8) 1.365(3); N(4)–C(12) 1.458(3); C(8)–N(5) 1.305(3); C(8)–C(11) 1.468(4); N(5)–N(6) 1.373(3); N(5)–C(10) 1.474(3); N(6)–C(9) 1.456(3); C(13)–O(1) 1.150(3); C(14)–O(2) 1.153(3). Selected bond angles (°): C(1)–Ni(1)–C(1) 109.38(9); C(13)–Ni(1)–C(14) 108.17(13); C(7)–Ni(1)–C(13) 106.65(11); C(7)–Ni(1)–C(14) 114.20(11); C(13)–Ni(1)–C(1) 113.02(10); C(1)–Ni(1)–C(14) 105.57(11); N(1)–C(1)–N(3) 101.96(19); N(6)–C(7)–N(4) 101.8(2).

3. Conclusion

1,2,4-Triazol-2-ium-5-ylidene complexes of Hg(II), Pd(II), Ni(II), Ni(0), Rh(I) and Ir(I) are readily accessible from the corresponding dicationic triazolium salts by one-pot deprotonation-complexation reactions. According to NMR and X-ray studies the metal–carbon bond lengths are in the range of typical metal–carbon single bonds suggesting that π-backbonding is negligible. The triazoliumylidene–Ni(0) complex has been synthesized by reduction of the corresponding Ni(II) complex with zinc in the presence of carbon monoxide. Due to their ionic character these carbene–metal complexes are extremely soluble in polar solvents including water; therefore promising applications in homogeneous catalysis can be envisaged [22].

4. Experimental

All reactions and manipulations were carried out under argon using standard Schlenk technique. Solvents were dried according to the appropriate method: CH_2Cl_2 with P_4O_{10}, MeCN and C_5H_{12} with CaH_2, tetrahydrofuran and Et_2O with sodium/benzophenone. NMR spectra were recorded on Brucker AC200, WM250 or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external reference. ^{31}P-NMR downfield chemical shifts are expressed with a positive sign relative to external 85% H_3PO_4. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer. Mass spectra were obtained on a Nermag R 10-10 instrument. Crystallographic data were collected on a STOE-IPDS diffractometer. The structures were solved by direct methods (SHELXS-96) and refined using the least-square method on F^2. Cyclic voltametric measurements were performed at room temperature (r.t.) using a purified argon atmosphere, MeCN as solvent, a scan rate of 100 mV s^{-1}, and a 0.1 M tetrabutylammonium hexafluorophosphate solution as the conducting salt.

4.1. *Dicationic 1,2,4-triazolium salts* ***2***

Methyl trifluoromethanesulfonate (30 mmol) was added to a solution of triazolium salt **1** [11] (10 mmol) in dichloroethane (25 ml). After 4 days of refluxing, the solid was filtrated and dried under vacuum. **2a**: yield: 95%, m.p. 194 °C. ^1H-NMR (C_3H_6O-d_6): δ 3.35 (s, 3H, CH_3C), 4.46 (s, 3H, CH_3N), 4.69 (s, 3H, CH_3N), 4.77 (s, 3H, CH_3N), 10.77 (s, 1H, H_{cycl}). ^{13}C-NMR (C_3H_6O-d_6): 10.5 (s, CH_3C), 35.9 (s, CH_3N), 36.3 (s, CH_3N), 38.0 (s, CH_3N), 120.3 (q, $^1J_{CF} = 320.1$ Hz, CF_3), 145.3 (s, CH_{cycl}), 157.3 (s, $C_{cycl}CH_3$). **2b**: yield: 71%, m.p. 180 °C. ^1H-NMR (CD_3CN): δ 4.08 (s, 3H, CH_3N), 4.20 (s, 3H, CH_3N), 4.46 (s, 3H, CH_3N), 7.8–8.1 (m, 5H, C_6H_5), 10.16 (s, 1H, H_{cycl}). ^{13}C-NMR (CD_3CN): 37.9 (s, CH_3N), 38.4 (s, CH_3N), 39.4 (s, CH_3N), 130.8, 132.0, 132.1, 137.3 (phenyl), 120.3 (q, $^1J_{CF} = 320.1$ Hz, CF_3), 147.3 (s, CH_{cycl}), 156.5 (s, C_{cycl}).

4.2. *Mercury(II) complex* ***4***

To a suspension of **2b** (430 mg, 0.50 mmol) in 21 ml THF–Me_2SO (20:1) mercury diacetate (160 mg, 0.50 mmol) was added. The mixture was stirred for 24 h at r.t. and then the brown microcrystalline complex **4** isolated by filtration (538 mg, 86%); m.p. 86–87 °C; ^1H-NMR (CD_3OD): δ 2.62 (s, 24H, Me_2SO), 4.25 (s, 6H, ^4J(H–Hg) = 8.5 Hz, NCH_3), 4.30 (s, 6H, NCH_3), 4.71 (s, 6H, ^4J(H–Hg) = 12.8 Hz, NCH_3), 7.9 (m, 10H, Ph); ^{13}C-NMR (CD_3OD): δ 38.8 (s, NCH_3), 39.1 (s, NCH_3), 40.7 (s, Me_2SO), 41.7 (s, NCH_3), 118.2 (s, Ph), 121.1 (q, ^1J(C–F) = 320 Hz, CF_3), 132.0 (s, Ph), 136.9 (s, Ph), 156.9 (s, J(C–Hg) = 86 Hz, *C*Ph), 183.8 (s, ^1J(C–Hg) = 3275 Hz, CHg).

4.3. *Palladium(II) and nickel(II) complexes* ***5a, b*** *and* ***6b***

To a suspension of **2** (1.1 mmol) and sodium iodide (320 mg, 2.2 mmol) in THF (20 ml) was added 0.55 mmol of palladium or nickel diacetate. The mixture was heated at reflux for 24 h to afford a precipitate. The solvent was removed by filtration and the powder washed with THF to afford the corresponding complexes.

Complex **5a**: yield: 60%, m.p. 206–212 °C (dec); ^1H-NMR (Me_2SO-d_6): δ 2.95 (s, 6H, CCH_3), 4.15 (s, 3H, NCH_3), 4.16 (s, 3H, NCH_3), 4.29 (s, 6H, NCH_3), 4.40 (s, 3H, NCH_3), 4.41 (s, 3H, NCH_3).

Complex **5b**: yield: 51%, m.p. 211–213 °C (dec); ^1H-NMR (Me_2SO-d_6): δ 4.10 (s, 3H, NCH_3), 4.13 (s, 3H, NCH_3), 4.21 (s, 6H, NCH_3), 4.49 (s, 3H, NCH_3), 4.53 (s, 3H, NCH_3), 7.9 (m, 10H, Ph); ^{13}C-NMR (Me_2SO-d_6): δ 37.2 (NCH_3), 38.3 (NCH_3), 39.9 (NCH_3), 130.1 (Ph), 130.9 (Ph), 134.5 (Ph), 152.4 (*C*Ph), 174.5 (CPd).

Complex **6b**: yield 85%, m.p. 311 °C (dec); ^1H-NMR (C_3H_6O-d_6): δ 4.41 (s, 3H, NCH_3), 4.42 (s, 3H, NCH_3), 4.49 (s, 3H, NCH_3), 4.54 (s, 3H, NCH_3), 4.84 (s, 3H, NCH_3), 4.88 (s, 3H, NCH_3), 7.9 (m, 10H, Ph); ^{13}C-NMR ($CD_3C(O)CD_3$): δ 37.0 (NCH_3), 37.9 (NCH_3), 38.4 (NCH_3), 130.5 (Ph), 130.8 (Ph), 134.8 (Ph), 153.4 (*C*Ph), 188.2 (CNi).

4.4. *Nickel(II) complex* ***6a***

To a suspension of **2a** (4.0 g, 9.4 mmol) and sodium iodide (1.41 g, 9.4 mmol) in THF (200 ml) was added a solution of nickel diacetate (0.83 g, 4.7 mmol) in THF (100 ml). The mixture was stirred for 40 h at r.t. A dark red precipitate was isolated by filtration and extracted with MeCN. After evaporation of the solvent **7a** (6.41 g, 79%) was obtained as a brown solid; m.p. 300–305 °C (dec); ^1H-NMR (C_3H_6O-d_6): δ 2.63 (s, 6H, CCH_3), 4.41 (s, 3H, NCH_3), 4.42 (s, 3H, NCH_3), 4.49 (s, 3H, NCH_3), 4.54 (s, 3H, NCH_3), 4.84 (s, 3H, NCH_3), 4.88 (s, 3H, NCH_3); ^{13}C-NMR (C_3H_6O-d_6): δ 13.9 (CCH_3), 36.1 (NCH_3), 37.6 (NCH_3), 38.5 (NCH_3), 121.1 (q, ^1J(CF) = 320.1 Hz), 154.8 (CCH_3), 187.6 (CNi).

4.5. *Rhodium(I) complex* ***7***

To a suspension of **2a** (456 mg, 1.1 mmol) and sodium iodide (160 mg, 1.1 mmol) in THF (40 ml) was added a solution of acetylacetonate dicarbonylrhodium (277 mg, 1.1 mmol) in THF (10 ml). The mixture was stirred for 2 days at 50 °C. The light brown powder obtained after concentration of the solution was isolated by filtration and washed several times with CH_2Cl_2 (432 mg, 70%). ^1H-NMR (Me_2SO-d_6): δ 2.96 (s, 3H, CCH_3), 4.20 (s, 3H, NCH_3), 4.28 (s, 3H, NCH_3), 4.47 (s, 3H, NCH_3); ^{13}C-NMR (Me_2SO-d_6): δ 10.5 (s, CCH_3), 35.2 (s,

NCH_3), 36.8 (s, NCH_3), 37.9 (s, NCH_3), 121.1 (q, $J(CF) = 320.1$ Hz, CF_3), 154.2 (s, $\mathit{C}CH_3$), 183.0 (d, $J(RhC) = 82.9$ Hz, CO), 188.1 (d, $J(RhC) = 42.2$ Hz, CRh); IR (KBr, cm^{-1}): 1975 (ν(CO)).

4.6. Iridium(I) complex **8**

To a suspension of **2a** (306 mg, 0.72 mmol) and sodium iodide (108 mg, 0.72 mmol) in THF (20 ml) was added a solution of acetylacetonate dicarbonyliridium (250 mg, 0.72 mmol) in THF (10 ml). The mixture was stirred for 2 days at 50 °C. After addition of Et_2O (30 ml) to the reaction mixture the precipitate that formed was isolated by filtration and washed with ether (346 mg, 74%). ^{1}H-NMR (CD_3CN): δ 2.73 (s, 3H, CCH_3), 4.04 (s, 3H, NCH_3), 4.05 (s, 3H, NCH_3), 4.29 (s, 3H, NCH_3); ^{13}C-NMR (CD_3CN): δ 11.6 (s, $\mathit{C}CH_3$), 36.5 (s, NCH_3), 38.1 (s, NCH_3), 38.8 (s, NCH_3), 122.1 (q, $J(CF) = 320.6$ Hz, CF_3), 154.7 (s, $\mathit{C}CH_3$), 169.0 (s, CIr), 183.7 (s, CO); IR (KBr); ν(CO): 1974 cm^{-1}.

4.7. Nickel(0) complex **9**

4.7.1. Method A

To a solution of complex **6** (200 mg, 0.23 mmol) and zinc powder (150 mg, 2.3 mmol) in oxygen-free MeCN (10 ml) an excess of gaseous carbon monoxide was introduced. The red solution turns to a pale yellow colour. The mixture was filtered and ether was added to the MeCN solution, complex **9** subsequently precipitating (73 mg, 48%). ^{1}H-NMR (CD_3CN): δ 2.73 (s, 3H, CCH_3), 3.78 (s, 3H, NCH_3), 3.99 (s, 3H, NCH_3), 4.00 (s, 3H, NCH_3); ^{13}C-NMR (CD_3CN): δ 11.0 ($C\mathit{CH_3}$), 35.7 (NCH_3), 36.9 (NCH_3), 37.5 (NCH_3), 152.8 ($\mathit{C}CH_3$), 199.9 (CNi), 200.4 (CO). IR (KBr, cm^{-1}): 1975 (ν(CO)); Anal. Calc. for $C_{16}H_{24}F_6N_6NiO_8S_2$. Calc. C, 28.89; H, 3.64; N, 12.63. Found: C, 28.99; H, 3.36; N, 12.39%.

4.7.2. Method B

To a mixture of nickel tetracarbonyl (2 ml, 10 mmol), pyridine (0.37 g, 4.7 mmol) and Et_3N (0.48 g, 4.7 mmol) in oxygen-free MeCN (40 ml), a solution of **2a** (1.90 g, 4.4 mmol) in MeCN (60 ml) was added drop-wise. The solution was stirred for 1 h at r.t. The solvent was evaporated to 2/3 of the initial volume and 200 ml of Et_2O was added. Compound **9** precipitated as yellow crystals (0.73 g, 25%).

4.8. X-ray measurements

Crystal data for all structures are presented in Table 1. All data were collected at low temperatures on a Stoe-IPDS diffractometer with Mo–K_α ($\lambda = 0.71073$ Å). All structures were solved by direct methods by means of SHELXS-97 [23] and refined with all data on F^2 by means of SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding

Table 1
Crystallographic data for **4**, **5a**, **6a** and **9**

	4	**5a**	**6a**	**9**
Empirical formula	$C_{30.5}H_{35.5}F_{12}HgN_6O_{15.5}S_5$	$C_{16}H_{30}I_4N_8Pd$	$C_{14}H_{24}F_6I_2N_6NiO_6S_2$	$C_{16}H_{24}F_6N_6NiO_8S_2$
Formula weight	1323.04	948.48	863.02	665.24
Temperature (K)	193(2)	193(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/m$	$P2_1/c$
Unit cell dimensions				
a (Å)	12.185(1)	7.876(1)	8.957(5)	14.465(4)
b (Å)	14.172(2)	17.521(1)	11.299(3)	9.740(2)
c (Å)	16.728(2)	11.157(1)	14.174(5)	18.631(5)
α (°)	67.49(1)	–	–	–
β (°)	76.72(1)	107.21(1)	93.57(5)	91.69(3)
γ (°)	73.93(1)	–	–	–
V (Å^3)	2539.3(5)	1470.7(2)	1431.7(10)	2623.8(11)
Z	2	2	2	4
Absorption coefficient	3.345	4.847	3.058	0.994
Crystal size (mm)	0.4 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.8 × 0.5 × 0.1	0.6 × 0.4 × 0.1
θ Range for data collection (°)	2.59–24.14	2.32–24.19	2.88–23.25	2.19–23.53
Reflections collected	14590	10727	5111	21131
Independent reflections	7530	2310	1058	3820
T_{min}/T_{max}	–	0.3714/0.5222	0.2305/0.7631	0.7292/0.8961
Parameter	730	138	106	360
wR_2 (all data)	0.1081	0.0712	0.1635	0.0753
$R_1[I > 2\sigma(I)]$	0.0404	0.0282	0.0636	0.0285
Largest difference peak and hole (e Å^{-3})	1.284/−2.218	0.533/−0.847	1.613/−1.317	0.347/−0.314

$R_1 = \Sigma\ ||F_o| - |F_c||\Sigma\ |F_o|$ and $wR_2 = (\Sigma\ w(F_o^2 - F_c^2)^2)/\Sigma\ w(F_o^2)^2)^{0.5}$.

model. Refinement of a disorder of the coordinated molecule of Me_2SO (0.58/0.42 for two positions for S and O) and the disorder of rotation of the CF_3 groups in two OTf anions (0.35/0.65 and 0.28/0.72) in **4** were realized with the help of 355 ADP and distances restraints.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 192692–192695 for complexes **4**, **5a**, **6a**, **9**, respectively. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk/conts/retrieving.html or the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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