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Cyclometalated Ruthenium Compounds Containing 2-(2′-Pyridyl)-4-methylphenyl and Benzo[*h*]quinolyl Ligands

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Keywords: Ruthenium / Cyclometalated ligands / Organometallic compounds / Transition metals

Transmetalation of $Hg(ptpy)_2$ [Hptpy = 2-(4-tolylpyridine) with Cp*Ru(NO)Cl_2 (Cp* = η^5-C_5Me_5)] gave [Cp*Ru(NO)(ptpy)]$_2$[Hg_2Cl_6] ([**1**]$_2$·Hg_2Cl_6) whereas that with [Cp*RuCl_2]$_x$ gave the dinuclear Ru^{II}–Ru^{IV} compound [Cp*Ru(μ-η^6:η^2-ptpy)RuCl_2Cp*][Hg_2Cl_6] (**2**). Treatment of Ru(3-phenylindenylid-1-ene)$Cl_2(PPh_3)_2$ with $Hg(ptpy)_2$ resulted in coupling of ptpy with the 3-phenylidenylid-1-ene ligand, and the formation of Ru(Ph-ind-ptpy)(PPh_3)Cl {Ph-ind-tpy = 3-phenyl-1-[2-(4-toyl)pyridyl]indenyl} (**3**), in which the chelated [Ph-ind-tpy]$^-$ ligand binds to Ru through the η^5-indenyl ring and the pendant pyridyl group. Treatment of [Ru$(CO)_2Cl_2$]$_n$ with [Hg(ptpy)Cl]$_2$ afforded [Ru(ptpy)$(CO)_2$]$_2$(μ-Cl)$_2$ (**8**). Irradiation of *cis*-[Ru$(bzq)_2(CO)_2$] (Hbzq = benzo[*h*]quinoline) with UV light in MeCN afforded *cis*-[Ru$(bzq)_2$(CO)(MeCN)] (**9**). Photolysis of *cis*-[Ru$(bzq)_2(CO)_2$] in THF in the presence of PPh_3 and pyridine (py) afforded *cis*-[Ru$(bzq)_2$(CO)(L)] [L = PPh_3 (**10**), py (**11**)]. The crystal structures of complexes **1**–**3**, **8**, and **10** have been determined.

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Introduction

Transition-metal complexes containing cyclometalated N^C ligands, notably 2-phenylpyridine (ppy), have attracted much attention because of their interesting photoluminescent properties[1] and their potential applications in organic synthesis[2] and bioinorganic chemistry.[3,4] Of note are cyclometalated Ir^{III} complexes, which have been used as phosphorescent dopants for organic light-emitting diodes,[5] chemical sensors,[6] and luminescent labels for biomolecules.[7] While the coordination chemistry of cyclometalated Ir^{III} compounds of the types [Ir$(ppy)_3$] and [Ir$(ppy)_2$(L)(X)][1,8–10] is well developed, the isoelectronic Ru^{II} analogues have received less attention.[9,10] This is in sharp contrast with cationic Ru^{II} complexes with 2,2′-bipyridyl (bpy) and polypyridyl ligands that exhibit rich redox- and photochemistry.[11] Owing to the anionic nature of ppy^-, it is anticipated that high-valence Ru–ppy complexes are more easily accessible than the bpy analogues. Recently, electron-rich Ru^{II} cyclometalated complexes have been used as mediators for electron transfer with horseradish peroxidase and glucose oxidase.[3]

To date, the most extensively explored Ru–ppy complexes are those supported by polypyridyl ligands.[12] Cyclometalated Ru^{II} N^C complexes containing η^6-arene[13] and phosphane[14,15] co-ligands have also been synthesized. These complexes were generally prepared by either transmetalation with organomercurials or direct cycloruthenation of N^CH ligands. In contrast to [M$(ppy)_2$]$^+$ (M = Rh, Ir), Ru^{II} bis-cyclometalated complexes are rather rare, the only structurally characterized example being *cis*-[Ru$(bzq)_2$$(CO)_2$] (Hbzq = benzo[*h*]quinoline).[16] As part of our continuing effort to explore the organometallic chemistry of high-valence Ru complexes, we set out to investigate the transmetalation between $Hg(ptpy)_2$ [Hptpy = 2-(4-tolyl)pyridine] and a variety of organoruthenium chloride compounds. Herein, we report on the syntheses and crystal structures of some cyclometalated ruthenium compounds containing the ptpy ligand. Furthermore, in order to prepare new Ru bis-cyclometalated complexes, photosubstitution of *cis*-[Ru$(bzq)_2(CO)_2$] with two-electron ligands has been studied.

Results and Discussion

Cyclometalated Ru Cp* Complexes

Treatment of Cp*Ru(NO)Cl_2 with $Hg(ptpy)_2$ in refluxing THF gave [Cp*Ru(ptpy)(NO)]$_2$[Hg_2Cl_6] ([**1**]$_2$·[Hg_2Cl_6]). Anion metathesis of [**1**]$_2$·[Hg_2Cl_6] with $NaPF_6$ in acetone afforded Hg-free [Cp*Ru(ptpy)(NO)][PF_6] (**1**[PF_6]) (Scheme 1). The formation of the chloromercurate anion [Hg_2Cl_6]$^{2-}$ from $HgCl_2$ and chloride salts is well documented.[13c,17,18] It may be noted that Djukic et al. previously reported that treatment of [(η^6-*p*-cymene)RuCl_2]$_2$ with Hg(ppy)Cl afforded [(η^6-*p*-cymene)Ru(ppy)Cl]·$HgCl_2$.[13c] The IR spectrum of [**1**]$_2$·[Hg_2Cl_6] shows the N–O band at about 1780 cm^{-1}, which is higher than that for [Cp*Ru(NO)Ph_2] (1755 cm^{-1}).[19] The structure of [**1**]$_2$·[Hg_2Cl_6] has been established by an X-ray diffraction study. The [Hg_2Cl_6]$^{2-}$

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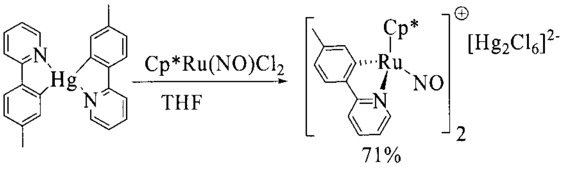
anion lies on a twofold rotation axis between two $[Cp^*Ru(ptpy)(NO)]^+$ cations. The molecular structure of the cation $[\mathbf{1}]^+$ is shown in Figure 1. The Ru–C(ptpy) [2.080(4) Å] and Ru–N [2.097(4) Å] distances and C(21)–Ru(1)–N(10) angle [77.95(17)°] in $\mathbf{1}^+$ are similar to those in $[(\eta^6\text{-}p\text{-cymene})Ru(ppy)Cl]\cdot HgCl_2$.[13c] The Ru–NO distance of 1.751(4) Å is shorter than that in $[Ru(ppy)(tpy)(NO)][PF_6]$ (tpy = 2,2′:6′,6′′-terpyridine) [1.826(4) Å],[12d] indicating the strong Ru-to-NO π-backbonding in $\mathbf{1}^+$. The N–O distance of 1.146(5) Å and the Ru–N–O angle of 174.4(4)° are normal by comparison with other linear nitrosyl compounds.[20]



$[\mathbf{1}]_2[Hg_2Cl_6]$

Scheme 1. Synthesis of $[\mathbf{1}]_2\cdot[Hg_2Cl_6]$.

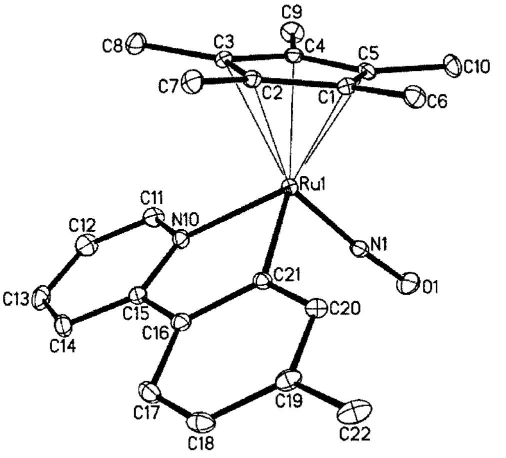
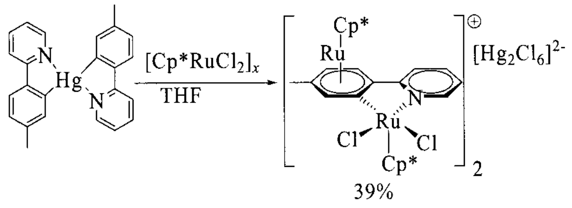


Figure 1. Perspective view of the cation $[Cp^*Ru(ptpy)(NO)]^+$ (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru–Cp*(centroid) 1.898(3), Ru(1)–N(1) 1.751(4), Ru(1)–N(10) 2.097(4), Ru(1)–C(21) 2.080(4), N(1)–O(1) 1.146(5); N(10)–Ru(1)–C(21) 78.0(2), N(1)–Ru(1)–N(10) 99.9(2), N(1)–Ru(1)–C(21) 94.5(2), Ru(1)–N(1)–O(1) 174.4(4).

Treatment of $[Cp^*RuCl_2]_x$ with $[Hg(ptpy)_2]$ afforded a dark green material from which air-stable dark crystals characterized as $[Cp^*Ru(\mu\text{-}ptpy)RuCp^*Cl_2]_2[Hg_2Cl_6]$ (**2**) were isolated (Scheme 2). The ^1H NMR spectrum shows two Cp* signals at $\delta = 1.87$ and 1.99 ppm, consistent with the solid-state structure. Upon binding to the Cp^*Ru^{II} fragment the resonant signals for the tolyl ring of the ptpy ligand are shifted to the upfield region ($\delta = 4.86$–5.36 ppm; cf. $\delta = 7.40$–7.72 ppm for $\mathbf{1}^+$). The identity of **2** has been established by a single-crystal X-ray diffraction study (Figure 2). The molecular structure of the cation $[Cp^*Ru(\mu\text{-}ptpy)RuCp^*Cl_2]^+$ in **2** consists of a $[Cp^*Cl_2Ru^{IV}(ptpy)]^+$ moiety, the 4-tolyl ring of which binds to the Cp^*Ru^{II} fragment in an η^6 fashion. It may be noted that a related bimetallic complex, $[(CO)_3Cr(\mu\text{-}ppy)Ru(\eta^6\text{-}p\text{-cymene})Cl]$, which contains a $\mu\text{-}\eta^2{:}\eta^6$-ppy ligand, has been synthesized recently.[13c] The geometry around Ru^{IV} in **2** is four-legged piano-stool whereas the Ru^{II}-containing moiety has a sandwich structure. The 4-tolyl and pyridine rings of the ptpy ligand are not coplanar, with a dihedral angle of about 12.3°. Cyclometalated Ru^{IV} complexes are rare. To the best of our knowledge, the only structurally characterized Ru^{IV} ppy complex is the mixed-valence Ru^{III}–Ru^{IV} compound $[\{Ru(ppy)(phen)Cl\}_2(\mu\text{-}O)][PF_6]$ (phen = 1,10-phenanthroline).[12e] The Ru^{IV}–Cp*(centroid) distance in **2** of 1.912(3) Å is comparable to reported Cp^*Ru^{IV} compounds (e.g. 1.916(4) Å for $[Cp^*Ru(\eta^2\text{-}Se_2P\mathit{i}Pr_2)(\eta^2\text{-}SeP\mathit{i}Pr_2)][PF_6]$),[21] but is obviously longer than the Ru^{II}–Cp*(centroid) distance [1.717(2) Å]. The Ru^{IV}–N and Ru^{IV}–C(ptpy) distances [2.132(7) and 2.081(8) Å, respectively] in **2** are similar to those in $\mathbf{1}^+$. The average Ru^{IV}–Cl distance of 2.417(2) Å is slightly longer than that of $[Cp^*Ru^{IV}Cl_2]_2[\mu\text{-}O]$ [2.356(8) Å].[22]



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Scheme 2. Synthesis of **2**.

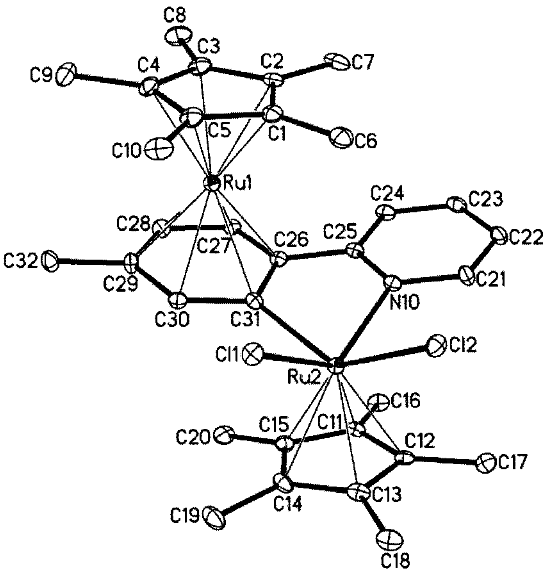
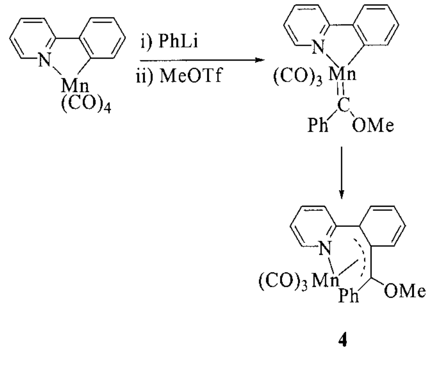


Figure 2. Perspective view of the cation $[Cp^*Ru(\mu\text{-}ptpy)RuCp^*RuCl_2]^+$ (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru(1)–Cp*(centroid) 1.717(2), Ru(1)–tolyl(centroid) 1.810(2), Ru(2)–N(10) 2.132(7), Ru(2)–C(31) 2.291(8), Ru(2)–Cl(1) 2.429(2), Ru(2)–Cl(2) 2.405(2), Ru(2)–Cp*(centroid) 1.912(3); N(10)–Ru(2)–C(31) 75.7(3), N(10)–Ru(2)–Cl(1) 129.1(2), N(10)–Ru(2)–Cl(2) 84.5(2), C(31)–Ru(2)–Cl(1) 82.1(2), C(31)–Ru(2)–Cl(2) 134.4(2), Cl(1)–Ru(2)–Cl(2) 79.40(7).

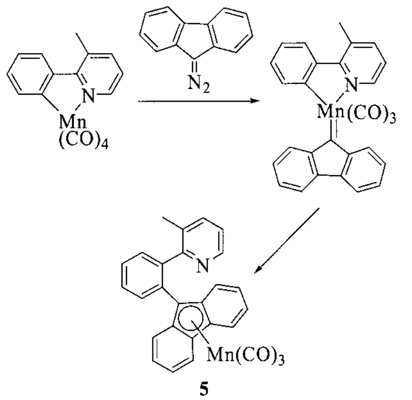
Transmetalation of [Hg(ptpy)$_2$] with Ru Carbene

Attempts to synthesize cyclometalated Ru complexes containing metal–carbon multiple bonds starting from Ru carbene and vinylidene species such as Ru(=CHPh)(PCy$_3$)$_2$-Cl$_2$ and Ru(=C=CHPh)(PCy$_3$)$_2$Cl$_2$ were unsuccessful. In most cases, dark intractable materials were obtained. However, treatment of Ru(3-phenylindenylid-1-ene)(PPh$_3$)$_2$Cl$_2$ with Hg(ptpy)$_2$ afforded an air-stable crystalline product that has been characterized as Ru(Ph-ptpy-ind)(PPh$_3$)Cl (**3**) (Ph-ptpy-ind = η^5:κN-3-phenyl-1-[2-(2-pyridyl)-4-tolyl]indenyl). It seems likely that **3** was formed by insertion of the indenylid-1-ene group into the Ru–C(ptpy) σ-bond. The insertion of carbene group into the M–C(N^C) bonds in M(N^C)(CO)$_4$ (M = Mn, Re) has been studied in detail by Djukic, Dötz, and Pfeffer and their co-workers.[23,24] It was found that treatment of Mn(CO)$_4$(ppy) with PhLi followed by addition of MeOTf led to insertion of the carbene ligand C(Ph)(OMe) into the Mn–C(ppy) bond and the formation of a η^3-benzyltricarbonyl Mn^I complex **4** (Scheme 3).[23a] On the other hand, thermolysis of Mn(CO)$_4$(Me-ppy) in the presence of 7-diazofluorene resulted in the insertion of the *exo*-alkylidene group into the Mn–C(ppy) bond. Subsequent cleavage of the Mn–N bond coupled with a series of haptotropic ring slippages afforded the Mn^I η^5-fluorenyl complex **5** (Scheme 4).[23e] On the basis of these results, we propose that the transmetalation of Ru(3-phenylindenylid-1-ene)(PPh$_3$)$_2$Cl$_2$ with Hg(ppy)$_2$ initially afforded a Ru^{II} indenylid-1-ene intermediate **6** (Scheme 5). Insertion of the indenylid-1-ene ligand into the Ru–C bond in **6** followed by haptotropic ring shifts, possibly via an η^3-allyl intermediate **7**, afforded **3**. Unlike the Mn(CO)$_4$(N^C) system, in which arenes tethered with cymantranes were formed,[23e] insertion of indenylidene into the Ru–C(ppy) bond led to formation of a chelated η^5-indenyl-ppy ligand, presumably because the PPh$_3$ ligand in **3** can be dissociated more easily than the carbonyl in the Mn counterparts.

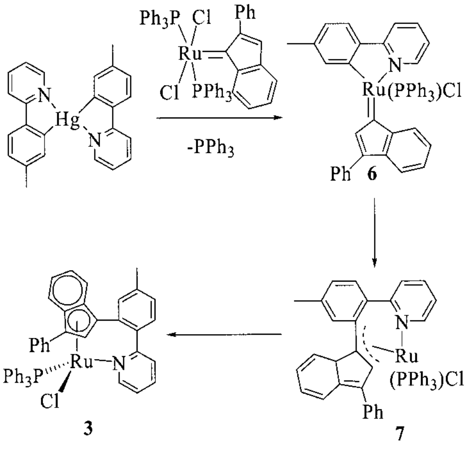


Scheme 3. Insertion of carbene into the Mn–C(ppy) bond.[23a]

The ^{31}P{^{1}H} NMR spectrum of **3** shows a singlet at δ = 33.1 ppm due to the PPh$_3$ ligand. The solid-state structure of **3** is shown in Figure 3. Similar to other Ru^{II} indenyl complexes, the Ru–C distances involving the bridging carbon atoms C(25) and C(29) [2.354(3) and 2.307(3) Å] are longer than those for C(26), C(27), and C(28) [2.105(3)–2.196(3) Å]. The Ru–P distance [2.2690(8) Å] is similar to



Scheme 4. Reaction of Mn(CO)$_4$(Me-ppy) with 7-diazofluorene.[23e]



Scheme 5. Proposed mechanism for the formation of **3**.

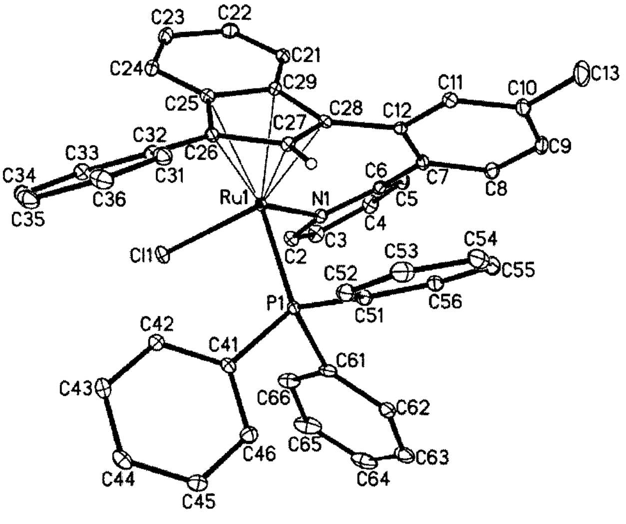
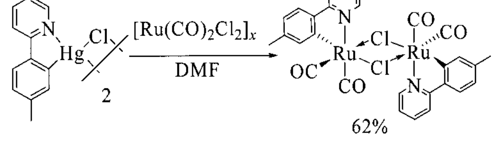


Figure 3. Perspective view of [Ru(Ph-ind-ptpy)(PPh$_3$)Cl] (**3**) (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru–indenyl(centroid) 1.849(3), Ru(1)–C(25) 2.354(3), Ru(1)–C(26) 2.196(3), Ru(1)–C(27) 2.125(3), Ru(1)–C(28) 2.105(3), Ru(1)–C(29) 2.307(3), Ru(1)–N(1) 2.169(3), Ru(1)–P(1) 2.2690(8), Ru(1)–Cl(1) 2.4575(8); Cl(1)–Ru(1)–N(1) 93.56(7), Cl(1)–Ru(1)–P(1) 93.30(3), N(1)–Ru(1)–P(1) 95.88(7).

that in $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)][ClO_4]$ [2.273(3) Å].[25] The pendant ptpy substituent of the indenyl group is significantly twisted and nonplanar with a dihedral angle between the 4-tolyl and pyridyl rings of about 36.8°.

Cyclometalated Ru Carbonyl Complexes

Treatment of $[Ru(CO)_2Cl_2]_x$ with $Hg(ptpy)_2$ afforded a yellow compound characterized as *cis*-$[Ru(ptpy)(CO)_2]_2(\mu\text{-}Cl)_2$ (**8**) in 18% yield. A higher yield (62%) of **8** was obtained when $[Hg(ptpy)(\mu\text{-}Cl)]_2$ was employed as the transmetalating agent (Scheme 6). The cyclometalated azobenzene analogue, $[Ru(N\^{}C)(CO)_2Cl]_2$ (N^CH = azobenzene), has been previously prepared by Bruce et al.[26] The IR spectrum of **6** shows $\nu(C{\equiv}O)$ at 2039 and 2104 cm^{-1}, indicative of the *cis* geometry of the carbonyl ligands. The molecular structure of **8** consisting of two symmetry-related $Ru(ptpy)(CO)_2Cl$ fragments is shown in Figure 4. The geometry around Ru is pseudo-octahedral, with the *cis*-disposed CO ligands opposite the pyridyl ring and chloride. The Ru–C(ptpy) distance [2.048(6) Å] in **8** is shorter than that in *cis*-$[Ru(bzq)_2(CO)_2]$ [2.161(5) Å],[16] in which both the Ru–C(bzq) bonds are *trans* to CO. The Ru–CO distances [1.888(7) and 1.830(7) Å] in **8** are comparable to those in *cis*-$[Ru(bzq)_2(CO)_2]$ [1.87(1) and 1.81(1) Å].[16b] The Ru–Cl(*trans* to 4-tolyl) [2.542(2) Å] is longer than Ru–Cl(*trans* to CO) [2.465(2) Å], suggesting that the σ 4-tolyl group has a stronger *trans* influence than carbonyl.



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Scheme 6. Synthesis of **8**.

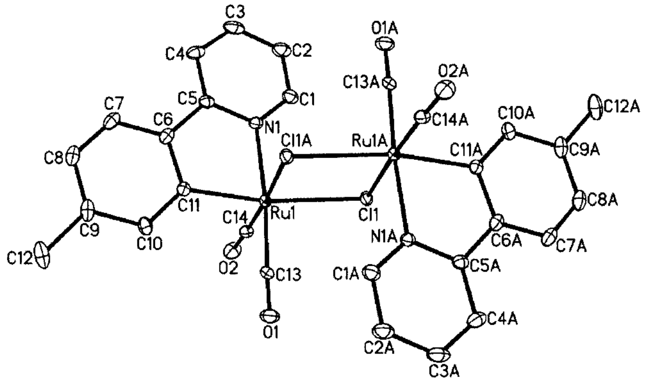
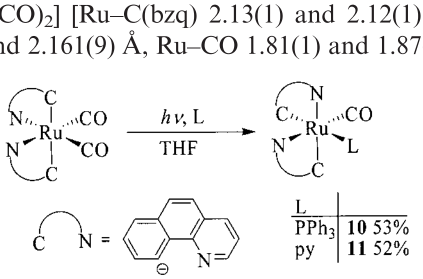


Figure 4. Perspective view of *cis*-$[Ru(ptpy)(CO)_2]_2(\mu\text{-}Cl)_2$ (**8**) (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru(1)–C(11) 2.048(6), Ru(1)–N(1) 2.139(5), Ru(1)–C(13) 1.888(7), Ru(1)–C(14) 1.830(7), Ru(1)–Cl(1) 2.542(2), Ru(1)–Cl(1A) 2.465(2); C(14)–Ru(1)–C(13) 88.0(3), C(14)–Ru(1)–C(11) 87.7(3), C(13)–Ru(1)–C(11) 94.5(3), C(14)–Ru(1)–N(1) 92.7(2), C(13)–Ru(1)–N(1) 174.5(2), C(11)–Ru(1)–N(1) 80.1(2), C(14)–Ru(1)–Cl(1A) 175.8(2), C(13)–Ru(1)–Cl(1A) 91.1(2), C(11)–Ru(1)–Cl(1A) 88.3(2), N(1)–Ru(1)–Cl(1A) 88.0(1), C(14)–Ru(1)–Cl(1) 101.1(2), C(13)–Ru(1)–Cl(1) 92.3(2), C(11)–Ru(1)–Cl(1) 169.1(2), N(1)–Ru(1)–Cl(1) 93.0(2), Cl(1A)–Ru(1)–Cl(1) 83.00(5), Ru(1A)–Cl(1)–Ru(1) 97.00(5) (symmetry code: $-x + 1, -y, -z + 1$).

Photosubstitution of *cis*-$[Ru(bzq)_2(CO)_2]$

Attempts to prepare Ru^{II} bis-cyclometalated complexes by treatment of $[Ru(CO)_2Cl_2]_x$ with excess $[Hg(ptpy)(\mu\text{-}Cl)]_2$ were unsuccessful. We then turned our attention to substitution of the reported compound *cis*-$Ru(bzq)_2(CO)_2$ with Lewis bases. Prolonged reaction of *cis*-$[Ru(bzq)_2(CO)_2]$ with excess PPh_3 in refluxing DMF afforded the mono carbonyl compound *cis*-$[Ru(bzq)_2(CO)(PPh_3)]$ in low yield (about 7%). The substitution of *cis*-$[Ru(bzq)_2(CO)_2]$ was found to be accelerated by UV light. Photolysis of *cis*-$[Ru(bzq)_2(CO)_2]$ in THF at room temperature afforded a highly air-sensitive, yellow species, presumably $Ru(bzq)_2(CO)(THF)$, which exhibited a C–O band at 2000 cm^{-1} in the IR spectrum. The MeCN adduct *cis*-$[Ru(bzq)_2(CO)(MeCN)]$ (**9**) was prepared similarly by photolysis of *cis*-$[Ru(bzq)_2(CO)_2]$ in MeCN and isolated as an air-sensitive red solid. Photosubstitution of *cis*-$[Ru(bzq)_2(CO)_2]$ with PPh_3 in THF afforded *cis*-$[Ru(bzq)_2(CO)(PPh_3)]$ (**10**) (Scheme 7). Compound **10** could also be prepared in good yield from **9** and PPh_3. An X-ray diffraction study revealed that the photosubstitution of *cis*-$[Ru(bzq)_2(CO)_2]$ led to a change in the stereochemistry of the complex. The two Ru–C(bzq) σ-bonds that are *trans* to each other in *cis*-$[Ru(bzq)_2(CO)_2]$ become mutually *cis* in **10** (vide infra). Similarly, the pyridine (py) adduct $Ru(bzq)_2(CO)(py)$ (**11**) was prepared by photosubstitution of *cis*-$[Ru(bzq)_2(CO)_2]$ with pyridine in THF. An attempt to prepare the bis-pyridine complex $Ru(bzq)_2(py)_2$ by photolysis of *cis*-$[Ru(bzq)_2(CO)_2]$ in neat pyridine was unsuccessful. Unlike **9** and **11**, **10** is air stable in both solutions and the solid state. The solid-state structure of **10** is shown in Figure 5. In contrast to *cis*-$[Ru(bzq)_2(CO)_2]$, both the Ru–N and Ru–C bonds for the bzq ligands adopt the *cis* arrangement. The Ru–C(bzq) [2.088(9) and 2.033(8) Å], Ru–N [2.157(7) and 2.194(7) Å], and Ru–CO [1.84(1) Å] distances in **10** are similar to those in *cis*-$[Ru(bzq)_2(CO)_2]$ [Ru–C(bzq) 2.13(1) and 2.12(1) Å, Ru–N 2.148(8) and 2.161(9) Å, Ru–CO 1.81(1) and 1.87(1) Å].[16b]



Scheme 7. Photosubstitution of *cis*-$[Ru(bzq)_2(CO)_2]$.

Attempts to prepare bis-cyclometalated Ru carbene species by reactions of **9** with alkynes and alkynols were unsuccessful. Treatment of **9** in THF with ethyl diazoacetate (EDA) resulted in a brown solution, which possibly contained a Ru carbene species given its ability in carbene

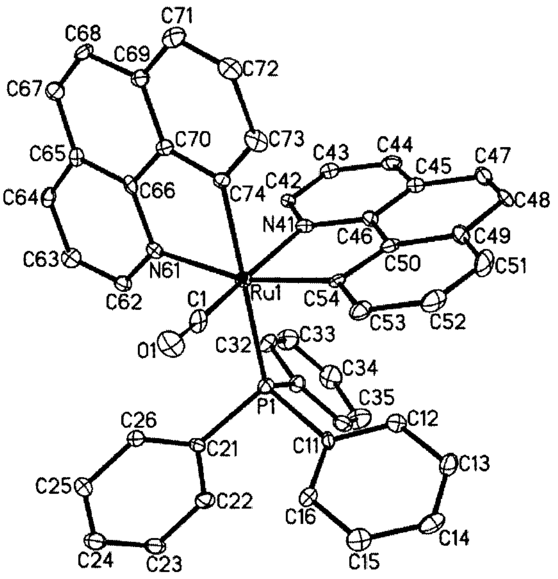


Figure 5. Perspective view of *cis*-[Ru(bzq)$_2$(CO)(PPh$_3$)] (**10**) (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru(1)–C(1) 1.84(1), Ru(1)–C(54) 2.033(8), Ru(1)–C(74) 2.088(9), Ru(1)–N(41) 2.157(7), Ru(1)–N(61) 2.194(7), Ru(1)–P(1) 2.385(3), C(1)–O(1) 1.14(1); C(1)–Ru(1)–C(54) 90.3(4), C(1)–Ru(1)–C(74) 87.9(4), C(54)–Ru(1)–C(74) 89.0(3), C(1)–Ru(1)–N(41) 168.7(3), C(54)–Ru(1)–N(41) 80.0(3), C(74)–Ru(1)–N(41) 86.2(3), C(1)–Ru(1)–N(61) 98.7(3), C(54)–Ru(1)–N(61) 165.0(3), C(74)–Ru(1)–N(61) 79.4(3), N(41)–Ru(1)–N(61) 89.7(3), C(1)–Ru(1)–P(1) 92.2(3), C(54)–Ru(1)–P(1) 91.6(3), C(74)–Ru(1)–P(1) 179.4(3), N(41)–Ru(1)–P(1) 93.8(2), N(61)–Ru(1)–P(1) 100.1(2), O(1)–C(1)–Ru(1) 173.8(9).

transfer (vide infra). Unfortunately, no crystalline products were isolated from the brown reaction mixture. A preliminary result showed that **9** is an active catalyst for cyclopropanation of styrene. For example, treatment of styrene with EDA in the presence of 5 mol-% of **9** afforded 2-phenylcyclopropane carboxylate in 76% yield along with a small amount of the homo-coupling product $C_2H_2(CO_2Et)_2$ (<5%). At present, efforts are being made to isolate the reactive cyclometalated Ru carbene species.

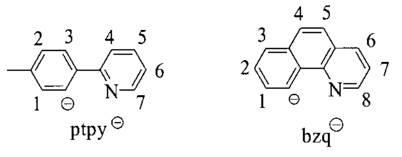
Conclusions

In summary, we have studied the transmetalation of [Hg(ptpy)$_2$] with a variety of organoruthenium compounds. Treatment of [Hg(ptpy)$_2$] with [Cp*RuCl$_2$]$_x$ afforded a mixed-valence Ru^{II}–Ru^{IV} complex that contains a μ-η^6:η^2 ptpy ligand. Transmetalation of [Hg(ptpy)$_2$] with [Ru(3-phenylindenylid-1-ene)(PPh$_3$)$_2$Cl$_2$] resulted in coupling of the carbene and the ptpy ligand and the formation of a Ru^{II} complex with a η^5:κ*N*-Ph-ind-ptpy ligand. The bis-cyclometalated Ru monocarbonyl complexes *cis*-[Ru(bzq)$_2$(CO)L] were prepared by photosubstitution of *cis*-[Ru(bzq)$_2$(CO)$_2$] with L (MeCN, PPh$_3$, and py).

Experimental Section

General: All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded with a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). Infrared spectra were recorded with a Perkin–Elmer 16 PC FT-IR spectrophotometer, and mass spectra with a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

The compounds [Cp*RuCl$_2$]$_x$,[27] [Cp*Ru(NO)Cl$_2$][28] (Cp* = η^5-C$_5$Me$_5$), [Ru(3-phenylindenylid-1-ene)(PPh$_3$)$_2$Cl$_2$],[29] *cis*-[Ru(bzq)$_2$(CO)$_2$],[16a] [Hg(ptpy)$_2$], and [Hg(ptpy)(μ-Cl)]$_2$[30] were synthesized according to literature methods. Hydrogen atom labeling schemes for cyclometalated ptpy$^-$ and bzq$^-$ ligands are shown below.



[Cp*Ru(ptpy)(NO)]$_2$[Hg$_2$Cl$_6$] ([1]$_2$·[Hg$_2$Cl$_6$]): A mixture of Cp*Ru(NO)Cl$_2$ (80 mg, 0.237 mmol) and Hg(ptpy)$_2$ (65 mg, 0.120 mmol) in THF (25 mL) was heated at reflux for 4 h, during which time the reaction color changed from green to orange. The solvent was pumped off, and the residue was washed with Et$_2$O and then extracted into CH$_2$Cl$_2$. Recrystallization from CH$_2$Cl$_2$/Et$_2$O gave orange crystals. Yield: 125 mg (71%). C$_{44}$H$_{50}$Cl$_6$Hg$_2$N$_4$O$_2$Ru$_2$·1/2THF (1520.0): calcd. C 36.5, H 3.65, N 3.69; found C 36.3, H 3.32, N 3.75. ^{1}H NMR ([D$_6$]acetone): δ = 2.04 (s, 30 H, Cp*), 2.61 (s, 6 H, CH$_3$), 7.40 (m, 4 H, H^1 and H^2), 7.72 (d, *J* = 6.7 Hz, 2 H, H^3), 8.13 (m, 4 H, H^5 and H^6), 8.45 (d, *J* = 7.2 Hz, 2 H, H^4), 8.94 (d, *J* = 6.2 Hz, 2 H, H^7) ppm. IR (KBr): ṽ = 1783 (s) [ν(NO)]. MS (FAB): *m*/*z* (%) = 435 ([Cp*Ru(ptpy)(NO)]$^+$), 406 ([Cp*Ru(ptpy)]$^+$ + 1).

[Cp*Ru(ptpy)(NO)][PF$_6$] (1[PF$_6$]): Na[PF$_6$] (1 equiv., 14 mg, 0.081 mmol) was added to a solution of [1]$_2$·[Hg$_2$Cl$_6$] (60 mg, 0.081 mmol) in acetone (20 mL) and the mixture was stirred at room temperature for 2 h and filtered through a Celite pad. The filtrate was evaporated to dryness and the residue recrystallized from acetone/Et$_2$O to give an orange crystalline solid. Yield: 48 mg (79%). C$_{22}$H$_{25}$F$_6$N$_2$OPRu (579.48): calcd. C 45.5, H 4.3, N 4.83; found C 46.1, H 4.26, N 4.77. ^{1}H NMR ([D$_6$]acetone): δ = 2.01 (s, 15 H, Cp*), 2.64 (s, 3 H, CH$_3$), 7.42 (m, 2 H, H^1 and H^2), 7.70 (d, *J* = 6.7 Hz, 1 H, H^1), 8.12 (m, 2 H, H^5 and H^6), 8.47 (d, *J* = 7.2 Hz, 1 H, H^4), 8.98 (d, *J* = 6.2 Hz, 1 H, H^7) ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 76.8 ppm. IR (KBr): ṽ = 1779 cm^{-1} [ν(NO)]. MS (FAB): *m*/*z* (%) = 435 (M$^+$ – PF$_6$), 405 (M$^+$ – PF$_6$ – NO).

[Cp*Ru(μ-ptpy)RuCl$_2$Cp*]$_2$[Hg$_2$Cl$_6$] (2): A mixture of [Cp*RuCl$_2$]$_x$ (85 mg, 0.138 mmol) and [Hg(ptpy)$_2$] (94 mg, 0.135 mmol) in THF (30 mL) was stirred at room temperature overnight and filtered. The filtrate was evaporated to dryness and the residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O to give dark red crystals, which were suitable for X-ray diffraction analysis. Yield: 54 mg (39%). [C$_{32}$H$_{40}$Cl$_5$HgNRu$_2$]$_2$·HgCl$_2$ (1136.65): calcd. C 33.8, H 3.52, N 1.23; found C 34.1, H 3.64, N 1.21. ^{1}H NMR ([D$_6$]acetone): δ = 1.87 (s, 30 H, Cp*), 1.99 (s, 30 H, Cp*), 2.46 (s, 6 H, CH$_3$), 4.86–5.03 (m, 4 H, H^1 and H^2), 5.36 (d, *J* = 6.2 Hz, 2 H, H^3), 7.86–7.94 (m, 4 H, H^5 and H^6), 8.63 (d, *J* = 7.1 Hz, 2 H, H^6), 9.08 (d, 2 H, *J* = 6.8 Hz, H^7) ppm. MS (FAB): *m*/*z* (%) 712 ([Cp*Ru(ptpy)RuCp*Cl$_2$]$^+$).

[Ru(Ph-ind-ptpy)(PPh$_3$)Cl] (3): Hg(ptpy)$_2$ (94 mg, 0.175 mmol) was added to a solution of Ru(3-phenylindenylid-1-ene)(PPh$_3$)$_2$Cl$_2$ (100 mg, 0.113 mmol) in THF (20 mL) and the mixture was stirred at room temperature overnight and filtered. The solvent was pumped off and the residue was washed with hexane/Et_2O and extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane gave red crystals. Yield: 37 mg (43%). $C_{45}H_{35}ClNPRu\cdot 1/2H_2O$ (766.29): calcd. C 70.5, H 4.74, N 1.83; found C 70.0, H 4.55, N 1.84. ^1H NMR ($CDCl_3$): δ = 2.17 (s, 3 H, CH_3), 5.30 (s, 1 H, CH), 6.88–7.49 (m, 27 H, Ph), 7.68 (d, J = 5.8 Hz, 1 H, H^4), 7.81 (m, 2 H, H^5 and H^6), 8.61 (d, J = 7.2 Hz, 1 H, H^7) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.1 ppm. MS (FAB): m/z (%) = 758 (M^+ + 1), 722 (M^+ – Cl).

[Ru(ptpy)(CO)$_2$]$_2$(μ-Cl)$_2$ (8): A mixture of $[Ru(CO)_2Cl_2]_x$ (80 mg, 0.35 mmol) and $[Hg(ptpy)(\mu\text{-}Cl)]_2$ (285 mg, 0.35 mmol) in DMF (15 mL) was heated at reflux overnight. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. The extract was concentrated to about 10 mL and excess Et_2O was added until a yellow solid was formed. The product was purified by column chromatography (silica) using CH_2Cl_2/acetone (9:1) as eluent. Recrystallization from CH_2Cl_2/Et_2O afforded pale yellowish green crystals. Yield: 68 mg (62%). $C_{28}H_{20}Cl_2N_2O_4Ru_2$ (721.50): calcd. C 46.6, H 2.77, N 3.88; found C 47.3, H 2.71, N 3.79. ^1H NMR ($CDCl_3$): δ = 2.21 (s, 6 H, CH_3), 6.92–7.03 (m, 4 H, H^1 and H^2), 7.14 (d, J = 6.2 Hz, 2 H, H^3), 7.76–7.96 (m, 4 H, H^5 and H^6), 8.49 (d, J = 7.4 Hz, 2 H, H^6), 9.17 (d, J = 7.0 Hz, 2 H, H^7) ppm. IR (KBr): $\tilde{\nu}$ = 2039, 2104 cm^{-1} [ν(C≡O)]. MS (FAB): m/z = 360 ([1/2M]$^+$).

***cis*-[Ru(bzq)$_2$(CO)(MeCN)] (9):** A solution of *cis*-[Ru(bzq)$_2$(CO)$_2$] (30 mg, 0.058 mmol) in MeCN (25 mL) was irradiated with a mercury lamp under N_2 for 1 h, during which time the color changed from pale yellow to dark red. The solvent was pumped off, and the residue was washed with Et_2O and then extracted with MeCN. Recrystallization from MeCN–CH_2Cl_2–Et_2O gave an air-sensitive dark red crystalline solid. Yield: 23 mg (76%). $C_{29}H_{19}N_3ORu\cdot CH_2Cl_2\cdot 1/2CHCl_3$ (671.19): calcd. C 54.6, H 3.23, N 6.26; found C 54.7, H 3.27, N 6.21. ^1H NMR (CD_3CN): δ = 6.69 (d, J = 7.5 Hz, 1 H, H^1), 6.87 (t, J = 7.5 Hz, 1 H, H^2), 6.98–7.03 (m, 1 H, H^1), 7.10–7.25 (m, 2 H, H^2 and H^3), 7.48–7.58 (m, 2 H, H^3 and H^7), 7.55 (t, J = 7.5 Hz, 1 H, H^7), 7.75 (s, 2 H, H^4), 7.82–7.87 (m, 2 H, H^5), 8.09 (d, J = 8.0 Hz, 1 H, H^6), 8.45 (d, J = 7.0 Hz, 1 H, H^8), 8.55 (d, J = 7.8 Hz, 1 H, H^6), 9.40 (d, J = 4.8 Hz, 1 H, H^8) ppm. IR (KBr): $\tilde{\nu}$ = 1890 [ν(C≡O)], 2014 [ν(C≡N)] cm^{-1}.

***cis*-[Ru(bzq)$_2$(CO)(PPh$_3$)] (10):** A mixture of *cis*-[Ru(bzq)$_2$(CO)$_2$] (50 mg, 0.097 mmol) and PPh_3 (51 mg, 0.195 mmol) in THF (25 mL) was irradiated with UV light under N_2 for 1 h, during which time the reaction color changed from pale yellow to dark yellow. The solvent was pumped off, and the residue was washed with Et_2O and extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/Et_2O/hexane gave yellow crystals that were suitable for X-ray diffraction. Yield: 38 mg (53%). $C_{45}H_{31}N_2OPRu\cdot 1/2H_2O$ (756.81): calcd. C 71.4, H 4.26, N 3.70; found C 71.3, H 4.29, N 3.68. ^1H NMR ($CDCl_3$): δ = 6.47–6.52 (m, 1 H, H^1), 6.66 (d, J = 5.0 Hz, 1 H, H^2), 6.92–7.00 (m, 2 H, H^1 and H^2), 7.02–7.18 (m, 15 H, PPh_3), 7.27–7.35 (m, 4 H, H^4 and H^5), 7.55–7.58 (m, 1 H, H^6), 7.67–7.99 (m, 4 H, H^3 and H^7), 8.12–8.15 (m, 1 H, H^8), 8.27 (d, J = 7.8 Hz, 1 H, H^6), 8.88 (d, J = 4.8 Hz, 1 H, H^8) ppm. IR (KBr): $\tilde{\nu}$ = 1912 cm^{-1} [ν(C≡O)].

[Ru(bzq)$_2$(CO)(py)] (py = pyridine) (11): A mixture of *cis*-[Ru(bzq)$_2$(CO)$_2$] (30 mg, 0.058 mmol) and pyridine (10 μL, 0.116 mmol) in THF (25 mL) was irradiated with UV light under N_2 for 1 h, during which time the color changed from pale yellow to orange red. The solvent was filtered and pumped off, and the residue was washed with Et_2O and then extracted with THF. Recrystallization from THF/Et_2O gave an air-sensitive, orange crystalline solid. Yield: 17 mg (52%). Despite several attempts, we have not been able to obtain satisfactory analytical data for the compound. ^1H NMR ([D$_6$]benzene): δ = 6.02–6.08 (m, 2 H, H^1), 6.85–6.89 (m, 2 H, H^2), 7.00 (m, 4 H, H^3 and H^7), 7.27–7.36 (m, 2 H, py), 7.56 (t, J = 7.4 Hz, 2 H, py), 7.62–7.69 (m, 4 H, H^4 and H^5), 7.76 (t, J = 8.6 Hz, 1 H, py), 8.37 (d, J = 4.8 Hz, 2 H, H^6), 9.31 (d, J = 7.4 Hz, 2 H, H^8) ppm. IR (KBr): $\tilde{\nu}$ = 1898 cm^{-1} [ν(C≡O)].

Table 1. Crystallographic data and structure refinement parameters for complexes [**1**]$_2$·[Hg$_2$Cl$_6$], **2**·HgCl$_2$, **3**·C$_4$H$_8$O, **8**, and **10**·C$_6$H$_{14}$·Et$_2$O.

Complex	[**1**]$_2$·[Hg$_2$Cl$_6$]	**2**·HgCl$_2$	**3**·C$_4$H$_8$O	**8**	**10**·C$_6$H$_{14}$·Et$_2$O
Empirical formula	$C_{22}H_{25}Cl_3HgN_2ORu$	$C_{32}H_{40}Cl_{5.5}Hg_{1.5}NRu_2$	$C_{49}H_{43}ClNOPRu$	$C_{28}H_{20}Cl_2N_2O_4Ru_2$	$C_{52}H_{48}N_2O_2PRu$
Formula mass	741.45	1136.65	829.33	721.50	864.96
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$Pbca$	$P2_1/n$
a [Å]	12.154(1)	10.1424(8)	11.6814(6)	11.850(1)	13.819(3)
b [Å]	10.854(1)	10.4592(8)	22.678(1)	13.583(1)	15.047(3)
c [Å]	19.439(2)	17.146(1)	14.7302(8)	16.832 (2)	20.414(4)
α [°]	90	96.572(1)	90	90	90
β [°]	107.583(1)	90.416(1)	92.447(1)	90	101.100(5)
γ [°]	90	102.348(1)	90	90	90
V [Å^3]	2444.5(3)	1764.2(2)	3898.7(4)	2709.0(5)	4165.0(2)
Z	4	2	4	4	4
D_{calcd} [g cm^{-3}]	2.015	2.140	1.413	1.769	1.379
T [K]	100(2)	100(2)	100(2)	298(2)	100(2)
μ [mm^{-1}]	7.235	7.791	0.551	1.350	0.459
F(000)	1416	1081	1712	1424	1796
Reflections collected	14064	14915	23888	14203	23644
Independent reflections	5719	7934	9230	3056	8456
R_{int}	0.0400	0.0303	0.0446	0.0966	0.0964
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0406, 0.0602	0.0519, 0.1384	0.0477, 0.1086	0.0536, 0.0904	0.0626, 0.1077
R_1, wR_2 (all data)	0.0732, 0.0686	0.0606, 0.1445	0.0686, 0.1184	0.0719, 0.1225	0.1112, 0.1800
Gof[c]	0.903	1.029	1.017	1.073	0.902

[a] $R_1 = \Sigma F_o - F_c|/\Sigma F_o$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^{22}]^{1/2}$. [c] Gof = $[\Sigma w(F_o - F_c)^2/(N_{obs} - N_{param})]^{1/2}$.

X-ray Crystallographic Study: A summary of crystallographic data and experimental details for complexes $[\mathbf{1}]_2\cdot[Hg_2Cl_6]$, $\mathbf{2}\cdot HgCl_2$, $\mathbf{3}\cdot C_4H_8O$, **8**, and $\mathbf{10}\cdot C_6H_{14}\cdot Et_2O$ are listed in Table 1. All intensity data were collected with a Bruker SMART-APEX diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.70173 Å). The data were integrated and sorted using SAINT v6.26A software[31] and were corrected for absorption by empirical methods. The structures were solved by direct methods and refined by full-matrix least-squares analyses on F^2. Calculations were performed using the SHELXTL[32] crystallographic software package. All non-hydrogen atoms were refined anisotropically with suitable restraints. Hydrogen atoms were generated geometrically (C–H = 0.95 Å) and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement.

CCDC-269638 to -269642 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.

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