(Diene)rhodium and -iridium Complexes of Pyridinophane Ligands

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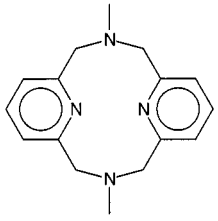
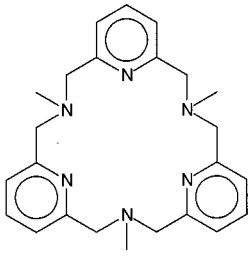
(Diene)rhodium(I) and -iridium(I) derivatives of the pyridinophane ligand L^4 and the analogous macrocycle L^6 have been prepared and characterized [diene = cyclooctadiene (COD) or norbornadiene (NBD)]. In all of the complexes, the ligand is coordinated in a κ^3-(amine)(pyridine)$_2$ fashion; a dynamic process, believed to be concerted, exchanges free and coordinated amine groups. $[L^4Ir(COD)]^+$ can be protonated at the amine nitrogen atom. It reacts with H_2O_2, but *only* in the presence of acid, to give an oxocyclooctenyl complex, formally a 4-e$^-$ oxidation product. X-ray structures of $[L^4Rh(COD)]PF_6$, $[L^6Rh(COD)]PF_6$, $[L^6Rh(NBD)]PF_6$, $[(L^4H)Ir(COD)](BF_4)_2$, and $[L^4Ir(C_8H_{11}O)](PF_6)_2$ are presented.

Introduction

Olefin oxidation at a transition metal center constitutes an important method for functionalizing hydrocarbons. Recent work by Klemperer,[1] Flood,[2] and ourselves[3–8] has shown that hard N- and O-donor ligands can be used to "trap" primary oxidation products such as metallaoxetanes and metalladioxolanes. The oxidation reactions have been found to be very sensitive to ligand variation. In order to explore these ligand effects further, we decided to investigate the (diene)rhodium and -iridium [diene = COD (cyclooctadiene), NBD (norbornadiene)] complexes of pyridinophane ligands L^4 and L^6.

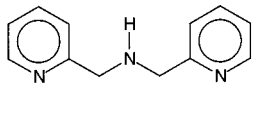


L^4

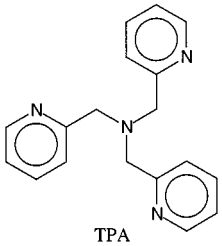


L^6

These ligands contain the same donor groups as the dipicolylamine (DPA) and tripicolylamine (TPA) ligands that we have studied previously,[5,6] but obviously have very different geometric constraints. Diene complexes are usually rather stable and thus provide a convenient starting point for further studies using more labile olefins. One Rh complex of L^4 has been reported,[9] but no Ir complexes. The coordination chemistry of L^6 appears to be relatively unexplored, and only complexes of two cryptand-like derivatives have been described.[10,11]



DPA

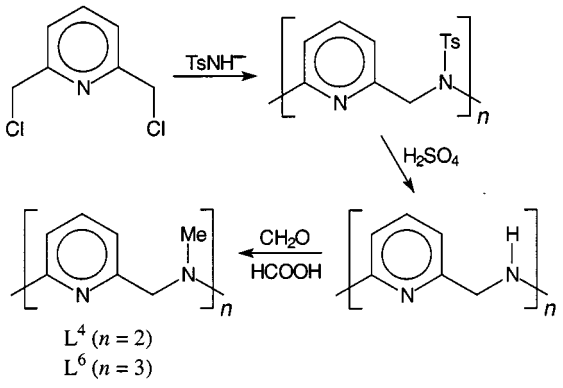


TPA

Results and Discussion

Synthesis

The syntheses of the ligands have been described by Bottino et al. (Scheme 1).[12] The ring-closure step in the syn-



Scheme 1. Ligand synthesis

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thesis always produces a mixture of bis- and tris(pyridine) ligands. The most convenient preparation of pure L^4 involves crystallization at the NH stage.[13] For the preparation of pure L^6, we separated the two components by chromatography at the *N*-tosyl stage; this was much less convenient and required large amounts of solvent.

Complexes of L^4 and L^6 were prepared by adding the ligand to a suspension of $[M(COD)Cl]_2$ (M = Rh, Ir) or $[Rh(NBD)Cl]_2$ in methanol. The products can be isolated as the PF_6, BF_4 or BPh_4 salts by precipitation, or as the chlorides by evaporation of the solvent.

Structure and Fluxionality

In all complexes the metal atom is coordinated to one amine nitrogen atom, two pyridine nitrogen atoms and the diene ligand. X-ray structures of $[L^4Rh(COD)]^+$, $[L^6Rh(COD)]^+$, and $[L^6Rh(NBD)]^+$ are shown in Figures 1, 2, and 3, respectively. The structures are all roughly square-pyramidal, with N_{amine} occupying the apical position. In $[L^4Rh(COD)]^+$, the methyl group at the noncoordinated amine group points away from the Rh atom. This is somewhat surprising, since in the only other complex of a κ^3-coordinated L^4 ligand reported to date $[L^4Mo(CO)_3]$[14] the methyl group points in the opposite direction.[15]

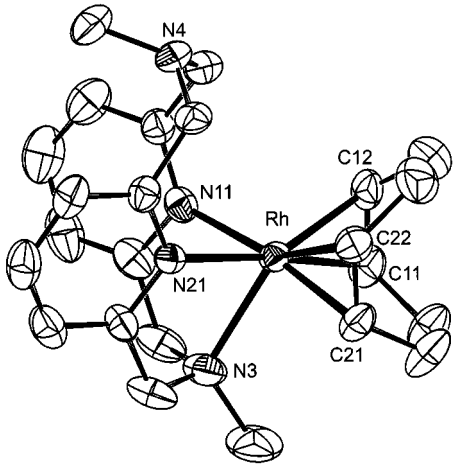


Figure 1. X-ray structure [40% TME (Thermal Motion Ellipsoids)] of $[L^4Rh(COD)]PF_6$; all hydrogen atoms and the counterion have been omitted; selected bond lengths [Å] and angles [°]: Rh−C11 2.105(7), Rh−C12 2.123(7), Rh−C21 2.119(8), Rh−C22 2.137(8), Rh−N11 2.183(6), Rh−N21 2.171(5), Rh−N3 2.336(7); N11−Rh−N21 75.9(2), N11−Rh−N3 77.0(2), N21−Rh−N3 77.0(2)

It is interesting to compare the structures of the L^4 and L^6 complexes with those of other tridentate N-donor ligands. We have recently reported the structures of several $Rh^I(COD)$ complexes of DPA-type ligands.[5] With one exception,[16] these all have $N_{py}-Rh-N_{py}$ angles of 87−92°. The $N_{py}-Rh-N_{py}$ angle in $[L^4Rh(COD)]^+$ is small (76°), undoubtedly because of steric constraints; in fact, it is close to the $N_{amine}-Rh-N_{py}$ angles (75−77° in our L^4 and L^6 complexes), and to the $N_{amine}-Rh-N_{amine}$ angles in $[Cn^*Rh(COD)]^+$ (77−80°) (Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane).[5] In contrast, the $N_{py}-Rh-N_{py}$ angles in the two L^6 complexes are normal (91° and 95°), showing that steric constraints are much less important there.

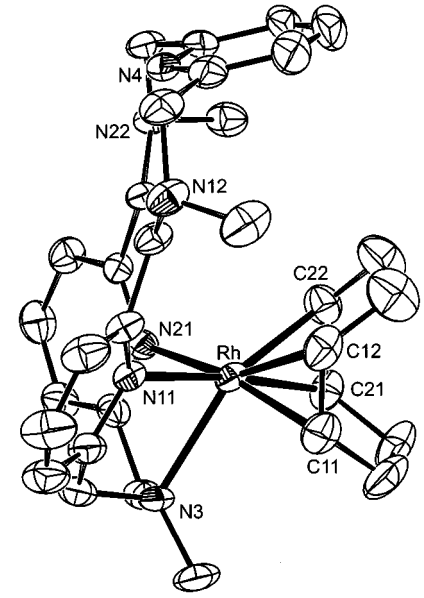


Figure 2. X-ray structure (40% TME) of $[L^6Rh(COD)]PF_6$; all hydrogen atoms and the counterion have been omitted; selected bond lengths [Å] and angles [°]: Rh−C11 2.124(5), Rh−C12 2.165(5), Rh−C21 2.101(5), Rh−C22 2.183(5), Rh−N11 2.311(4), Rh−N21 2.176(4), Rh−N3 2.343(4); N11−Rh−N21 91.48(14), N11−Rh−N3 75.86(14), N21−Rh−N3 75.15(15)

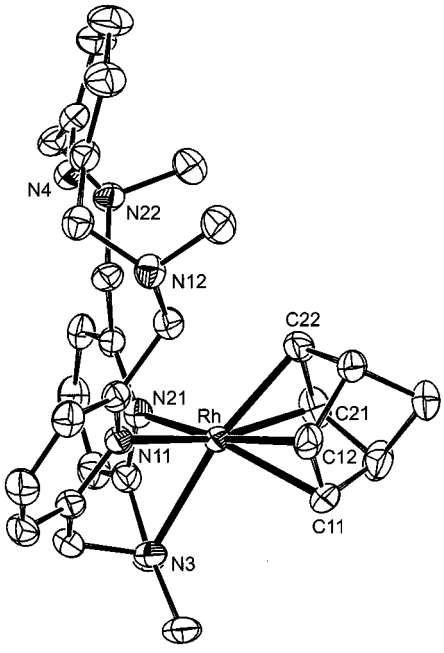
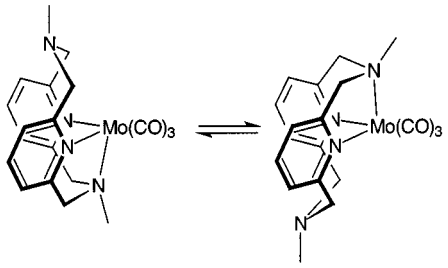


Figure 3. X-ray structure (40% TME) of $[L^6Rh(NBD)]PF_6$(acetone); all hydrogen atoms, the counterion and the acetone molecule of crystallization have been omitted; selected bond lengths [Å] and angles [°]: Rh−C11 2.152(4), Rh−C12 2.148(4), Rh−C21 2.054(4), Rh−C22 2.079(4), Rh−N11 2.310(3), Rh−N21 2.154(3), Rh−N3 2.278(3); N11−Rh−N21 94.71(12), N11−Rh−N3 75.95(12), N21−Rh−N3 74.84(12)

Ligand L^4 seems to be preorganized for κ^4 coordination. The κ^3-coordinated Mo complex mentioned above displays fluxional behaviour involving exchange of the two amine nitrogen atoms (Scheme 2) with activation parameters $\Delta H^{\ddagger} = 13.9$ kcal/mol, $\Delta S^{\ddagger} = -0.8$ cal/mol·K.



Scheme 2

The strongly broadened 1D ^{1}H NMR spectra and the negative cross-peaks in the NOESY spectra of our diene complexes indicate a similar fluxionality. The situation is complicated here by the occurrence of another fluxional process, namely diene rotation (Scheme 3). Diene rotation is common in five-coordinate complexes and would therefore be expected here; it exchanges the "top" and "bottom" halves of the diene ligand. Amine exchange would also exchange the diene halves; thus, the rate of diene rotation as determined by NMR includes a contribution from amine exchange. Variable-temperature NMR studies and full-spectrum NMR fits[17] were used to determine rate constants for $[L^4Rh(COD)]^+$, $[L^4Ir(COD)]^+$, and $[L^6Rh(COD)]^+$; the resulting activation parameters are shown in Table 1.

For the L^4 complexes, the total rate of COD rotation is significantly faster than the amine exchange in the temperature range of 0 to 100 °C, demonstrating that both processes indeed contribute. Interestingly, amine exchange has a lower activation *enthalpy*, but is still the slower process because of its more negative activation *entropy*. Since COD rotation is unlikely to be a dissociative process, these results

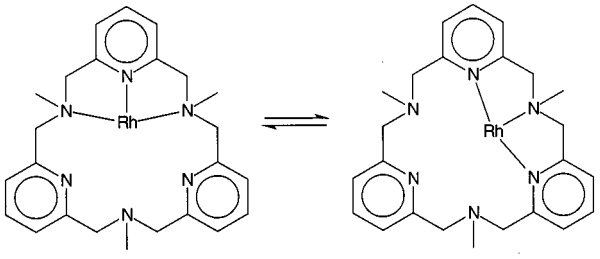
Table 1. Activation parameters for fluxionality of $LM(COD)^+$ complexes

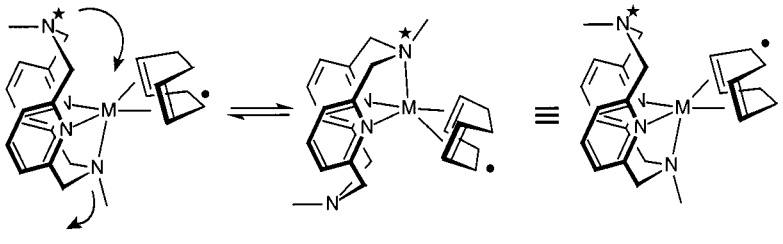
Complex	Amine exchange[a] [b]		COD rotation[a] [b]	
	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$[L^4Rh(COD)]PF_6$	12.0±0.3	−11.0±1.0	15.7±1.0	3.2±3.1
$[L^4Ir(COD)]PF_6$	14.0±0.2	−6.7±0.7	22.8±1.5	18.2±4.4
$[L^6Rh(COD)]PF_6$	11.8±0.3	−10.3±0.9		

[a] $\Delta H^{\ddagger}$ [kcal/mol], $\Delta S^{\ddagger}$ [cal/mol·K]. [b] Error margins are 1σ limits from Eyring fits.

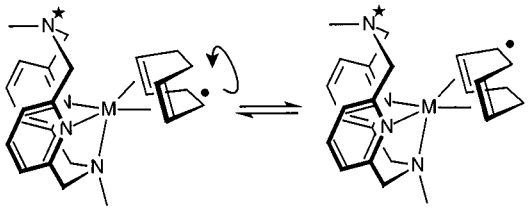
suggest that metal−amine bond dissociation and formation occur simultaneously. Amine exchange is only slightly slower for Ir than for Rh, which agrees with this interpretation; for a dissociative process, the Ir analogue should have a much higher barrier.

For $[L^6Rh(COD)]^+$, COD rotation is always fast on the NMR timescale. The activation parameters for movement of the metal atom around the ring are similar to those found for amine exchange in $[L^4Rh(COD)]^+$, suggesting a similar mechanism involving repeated amine/pyridine exchange at Rh. The metal atom thus presumably moves between κ^3-(amine)(pyridine)$_2$ and κ^3-(amine)$_2$(pyridine) compartments of the macrocycle; the observed preference for the κ^3-(amine)(pyridine)$_2$ compartment suggests that this is the stronger donor site. Even at 100 °C, the two faces of the ring remain inequivalent, implying that the Rh(COD) fragment cannot move *through* the ring.





amine exchange



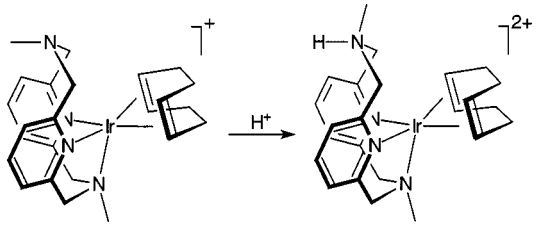
COD rotation

Scheme 3

Since L^6 has six N-donor atoms, one might wonder whether dinuclear complexes could be formed, in which one metal atom would occupy a κ^3-(amine)(pyridine)$_2$ compartment and the other a (less favourable) κ^3-(amine)$_2$(pyridine) compartment. However, treatment of L^6 with excess [Rh(diene)Cl]$_2$ produces the mononuclear complex as the only product. Possibly, there would be too much repulsion between the two diene fragments in a dinuclear complex. Also, the nitrogen lone pairs in the X-ray structures of [L^6Rh(COD)]$^+$ and [L^6Rh(NBD)]$^+$ are oriented in an unfavourable manner for coordination to the κ^3-(amine)$_2$(pyridine) compartment, as shown in Figures 2 and 3. We therefore conclude that formation of dinuclear complexes of L^6 is unlikely.

Protonation and Oxidation

Surprisingly, [L^4Ir(COD)]$^+$ reacts with H_2O_2 *only* in the presence of acid. Therefore, protonation was also investigated separately. Addition of a diethyl ether solution of HBF_4 to a solution of [L^4Ir(COD)]$^+PF_6$ in methanol produced a colourless solution. Evaporation of the solvent and dissolution of the product in methanol gave a yellow solution, from which red crystals precipitated overnight. The X-ray structure (Figure 4) shows these crystals to have the composition [(L^4H)Ir(COD)]$^+(BF_4)_2$; evidently, the lower solubility of the BF_4 salt resulted in selective precipitation of the complex with this counterion. Protonation has occurred on the dangling amine nitrogen atom. The hydrogen atom was located and refined; additional proof for protonation at the nitrogen atom comes from the C−N−C angles at the nitrogen atom (av. 110.2°), which are similar to those of the metal-coordinated nitrogen atoms in [(L^4H)Ir(COD)]$^+(BF_4)_2$ (av. 110.1°) and [L^4Rh(COD)]PF_6 (av. 109.9°) and definitely smaller than those around the dangling nitrogen atom in [L^4Rh(COD)]PF_6 (av. 115.6°). The methyl group on the ammonium nitrogen atom is now in the expected position, pointing towards the Ir atom; the ammonium proton forms a hydrogen bond with a fluorine atom of a BF_4 group. Apart from this, the structure of the dication is fairly similar to that of the unprotonated monocation [L^4Rh(COD)]$^+$.



Addition of excess H_2O_2 to a solution of [L^4Ir(COD)]$^+$ and 1 equiv. of acid results in a fast reaction to give an oxocyclooctenyl complex [L^4Ir($C_8H_{11}O$)]$^{2+}$. This is a net 4-e$^-$ oxidation and we were unable to detect any intermediates by NMR; 1 equiv. of acid is consumed, but if only 0.5 equiv. of acid is used, half of the starting material is recovered unchanged. Crystals suitable for X-ray diffraction were obtained from acetone; they were found to contain

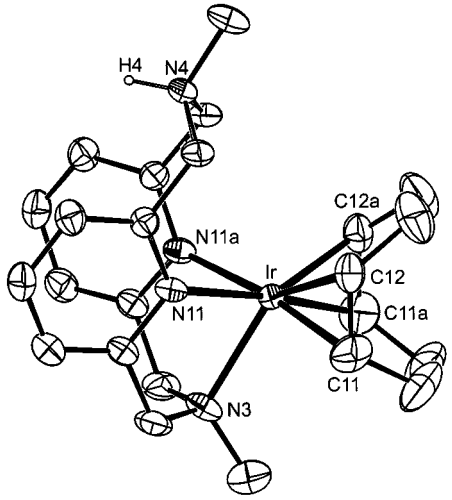
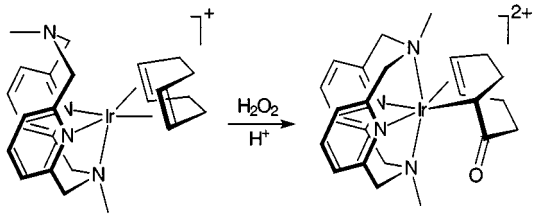


Figure 4. X-ray structure (50% TME) of [(L^4H)Ir(COD)]$(BF_4)_2$; all hydrogen atoms (except 4) and the counterion have been omitted; selected bond lengths [Å] and angles [°]: Ir−C11 2.091(7), Ir−C12 2.112(7), Ir−N11 2.169(5), Ir−N3 2.301(7); N11−Ir−N11a 74.6(3), N11−Ir−N3 77.9(2)

one molecule of diacetone alcohol of crystallization. The structure (Figure 5) shows that the ligand is now κ^4-coordinated. Compared with those in the Rh^I(COD) and Ir^I(COD) complexes described above, the Ir−N distances in this Ir^{III} derivative are shorter and the Ir−olefin distances longer, as expected. Perhaps somewhat surprisingly, all Ir−N distances are significantly shorter (by ca. 0.1 Å) than the corresponding Rh−N distances in [L^4RhCl_2]$^+$.[9]



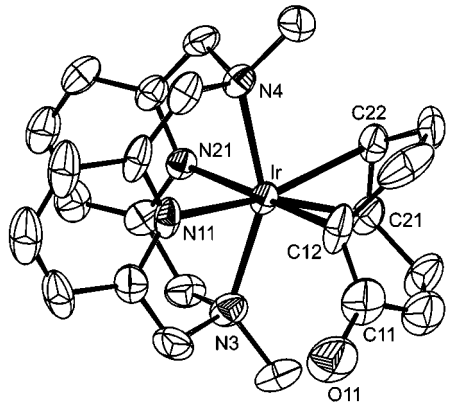
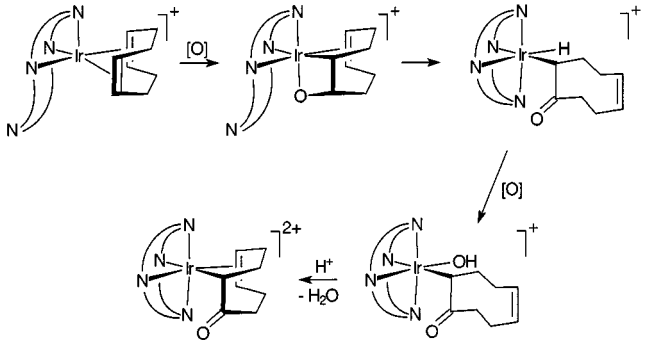


Figure 5. X-ray structure (30% TME) of [L^4Ir($C_8H_{11}O$)]$(PF_6)_2$(diacetone alcohol); all hydrogen atoms, the counterion and the molecule diacetone alcohol of crystallization have been omitted; selected bond lengths [Å] and angles [°]: Ir−C12 2.124(11), Ir−C21 2.242(10), Ir−C22 2.247(10), Ir−N11 2.031(8), Ir−N21 2.093(7), Ir−N3 2.213(10), Ir−N4 2.211(8), C11−O11 1.275(17); N11−Ir−N21 79.1(3), N11−Ir−N3 79.6(4), N21−Ir−N3 78.7(3), N11−Ir−N4 79.2(4), N21−Ir−N4 79.3(3), N3−Ir−N4 151.8(3)

Oxocyclooctadiene and oxoalkyl-allyl ligands somewhat similar to ours were obtained by Klemperer in the O_2 oxidation of Cp*Ir(COD).[18] He attributed their formation to a radical (autoxidation) mechanism; the reaction required rather drastic conditions. Since ligands, conditions and oxidants are different in our case, it is difficult to draw parallels between the two systems.

We have found that COD coordinated to Rh can be oxidized to an 9-oxabicyclo[4.2.1]nona-2,5-diyl fragment, presumably via a metallaoxetane intermediate.[3,5] (COD)Ir complexes can also be oxidized to oxetanes.[1,2,19] In both cases, the products rearrange to hydroxycyclooctenediyl complexes. In addition, we have observed that unsubstituted oxetanes can decompose to aldehydes, and can be oxidized to formylmethyl complexes.[8] On the basis of analogy, one possible mechanism for the formation of the oxocyclooctenyl complex could involve further oxidation of an initially formed metallaoxetane, represented schematically in Scheme 4.



Scheme 4

The change in ligand coordination mode from κ^3 to κ^4 might be important here; it could result in displacement of the unchanged C=C bond from the metal atom, thus facilitating further reaction of the oxetane by relieving geometric constraints. Since we have not been able to observe any intermediates, we feel that further speculation on details of this reaction is not warranted.

The most interesting aspect of the H_2O_2 oxidation chemistry is probably the role of acid. Activation of H_2O_2 by acid is relatively common, but the H_2O_2 oxidation of $[(DPA)Rh(COD)]^+$ and $[(N\text{-Bu-DPA})Rh(COD)]^+$ does not require the addition of acid.[5] It might be that for the L^4 ligand, with substituents in the 6-positions of the pyridine rings, the increased steric hindrance prevents or slows down direct oxidation by H_2O_2. The isolation of the amine-protonated Ir complex makes it tempting to suggest that such a protonated species might also might also play a role in the oxidation by, for example, activating H_2O_2 near the metal centre, assisting in the first step of Scheme 4.

Conclusions

(Diene)rhodium and -iridium complexes of L^4 and L^6 pyridinophane ligands have five-coordinate structures in which the ligand is bound in a κ^3-(amine)(pyridine)$_2$ fashion. All Rh and Ir complexes are fluxional and show movement of the (diene)metal fragment over the ligand. Oxidation of $[L^4Ir(COD)]^+$ by H_2O_2 requires addition of acid, and then gives the oxocyclooctenyl complex in a net 4-e$^-$ oxidation reaction. In the absence of H_2O_2, acid protonates the dangling amine ligand; an amine-protonated species *might* also play a role in the oxidation reaction.

Experimental Section

General: All synthesis involving air-sensitive compounds were carried out by using standard Schlenk techniques. All solvents were distilled under nitrogen prior to use. Starting materials were prepared by literature methods: L^4/L^6,[12] $[Rh(COD)Cl]_2$,[20] $[Rh(NBD)Cl]_2$,[21] $[Ir(COD)Cl]_2$.[22] All other reagents were commercial products.

$[L^4Rh(COD)]PF_6$: $[Rh(COD)Cl]_2$ (13 mg, 0.026 mmol) was added to a solution of L^4 (14 mg, 0.052 mmol) in methanol (6 mL). The mixture turned yellow. After stirring for 1 h, the solution was filtered, and a solution of KPF_6 (40 mg, 0.22 mmol) in methanol (4 mL) was added. The mixture was concentrated to half its volume in vacuo, after which a yellow solid precipitated. The supernatant was removed with a Pasteur pipette. The resulting solid was washed with methanol (3 × 3 mL) and dried in vacuo. Yield: 0.35 g (75%). $[L^4Rh(COD)]PF_6$ is a yellow, air-stable solid. ^{1}H NMR (500 MHz, [D$_6$]acetone, 213 K): δ = 7.71 (t, J = 7.7 Hz, 2 H, py H_4), 7.36 (d, J = 7.7 Hz, 2 H, py H_3), 7.23 (d, J = 7.7 Hz, 2 H, py H_5), 6.22 (d, J = 14.0 Hz, 2 H, NCH_2), 4.97 (d, J = 17.0 Hz, 2 H, NCH_2), 4.49 (d, J = 14.0 Hz, 2 H, NCH_2), 4.30 (d, J = 17.0 Hz, 2 H, NCH_2), 3.79 (s, 3 H, CH_3), 2.89 (br, 2 H, C=CH), 2.59 (br, 2 H, C=CH), 2.44 (m, 2 H, =CCH_2), 2.27 (s, 3 H, CH_3), 1.94 (m, 2 H, =CCH_2), 1.76 (m, 2 H, =CCH_2), 1.61 (m, 2 H, =CCH_2). ^{1}H NOESY (200 MHz, [D$_6$]acetone, 298 K, exchange cross-peaks): δ = (7.23⇄7.36, Py-$H_{3,5}$), (4.97⇄6.22, NCH_2), (4.30⇄4.49, NCH_2), (3.5⇄4.1, C=CH), (2.27⇄3.79, CH_3). At this temperature all ligand signals except that of py-H_4 are severely broadened. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 297 K): δ = 159 (2 C, py C_6), 158 (2 C, py C_2), 138 (2 C, py C_4), 126 (2 C, py C_5), 122 (2 C, py C_3), 80.7 (br, 2 C, =CH), 67.1 (2 C, NCH$_2$), 66.2 (br, 2 C, =CH), 65.0 (2 C, NCH_2), 51.8 (1 C, CH$_3$), 38.7 (1 C, CH$_3$), 32.6 (br, 2 C, = CHCH$_2$−), second =CHCH$_2$ obscured by acetone signal. FAB$^+$ MS (BPh$_4$ salt): m/z = 370 $[L^4Rh - H]^+$, 479 $[L^4Rh(COD)]^+$. IR (KBr): $\tilde{\nu}$ = 2976, 2943, 2906, 2895, 2852, 1603, 1463, 1450, 1105, 1035, 989, 874, 839, 771 cm^{-1}. $C_{24}H_{32}F_6N_4PRh$ (624.41): calcd. C 46.17, H 5.17, N 8.97; found C 46.42, H 4.91, N 8.61.

$[L^4Rh(NBD)]PF_6$: $[Rh(NBD)Cl]_2$ (107 mg, 0.23 mmol) was added to a solution of L^4 (125 mg, 0.47 mmol) in methanol (3 mL). The resulting yellow solution was stirred for 1 h. Upon addition of a solution of KPF_6 (343 mg, 1.86 mmol) in methanol (4 mL), a yellow solid precipitated. The solid was filtered off, washed with methanol (3 × 5 mL) and dried in vacuo. Yield: 215 mg (76%). ^{1}H NMR (500 MHz, [D$_6$]acetone, 273 K): δ = 7.60 (t, J = 7.8 Hz, 2 H, Py-H_4), 7.25 (d, J = 7.8 Hz, 2 H, Py-H_3), 7.15 (d, J = 7.8 Hz, 2 H, Py-H_5), 6.26 (d, J =14 Hz, 2 H, NCH_2), 4.96 (d, J = 16.0 Hz, 2 H, NCH_2), 4.47 (d, J = 14.0 Hz, 2 H, NCH_2), 4.34 (d, J = 16.0 Hz, 2 H, NCH_2), 4.11 (s, 3 H, CH_3), 3.99 (s, 2 H, NBD CH$_2$), 3.54 (m, 4 H, NBD =CH), 2.38 (s, 3 H, CH_3), 1.19 (s, 2 H, NBD =CCH). ^{1}H NOESY (200 MHz, [D$_6$]acetone, 298 K, exchange cross-peaks): δ = (7.15⇄7.19, Py-$H_{3,5}$), (5.02⇄6.23, NCH_2), (2.43⇄4.15, CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 297 K): δ = 159 (2 C, py C_2), 158 (2 C, py C_6), 137 (2 C, py C_4), 125 (2 C, py C_3), 121 (2 C, py C_5), 67.2 (2 C, NCH_2), 65.6 (2 C, NCH_2), 58.3 (4 C, NBD =C), 52.8 (1 C, NBD CH_2), 47.5 (1 C, CH_3), 39.4 (1 C, CH_3), 39.3 (2 C, NBD =CCH). FAB$^+$-MS: m/z = 370 [L^{4}Rh − H]$^+$, 463 [L^{4}Rh(NBD)]$^+$. IR (KBr): ṽ = 3004, 2941, 2892, 2861, 2813, 1601, 1573, 1464, 1449, 1430, 1305, 1168, 1101, 1034, 990, 968, 885, 839, 772, 557 cm^{-1}. We did not obtain a satisfactory elemental analysis for this complex: $C_{23}H_{28}F_6N_4PRh$ (608.37): calcd. C 45.41, H 4.64, N 9.21; found C 43.67, H 4.74, N 8.78.

[L^{6}Rh(COD)]PF$_6$: [Rh(COD)Cl]$_2$ (62 mg, 0.13 mmol) was added to a solution of L^6 (100 mg, 0.25 mmol) in methanol (10 mL). After the mixture had been stirred for 1 h, a solution of KPF_6 (184 mg, 1.0 mmol) in methanol (4 mL) was added. The reaction mixture was concentrated to half its volume in vacuo, after which a yellow solid precipitated. The product was filtered off, washed with methanol (3 × 2 mL) and dried in vacuo. Yield: 150 mg (79%). ^1H NMR (500 MHz, [D$_6$]acetone, 273 K): δ = 7.95 (t, J = 7.4 Hz, 1 H, py H_4), 7.92 (t, J = 7.4 Hz, 2 H, py H_4), 7.86 (d, J = 7.4 Hz, 2 H, py H_3), 7.50 (d, J = 7.4 Hz, 2 H, py H_5), 7.38 (d, J = 7.4 Hz, 2 H, py $H_{3,5}$), 5.07 (d, J = 17.0 Hz, 2 H, NCH_2), 4.96 (d, J = 17.0 Hz, 2 H, NCH_2), 4.57 (d, J = 15.0 Hz, 2 H, NCH_2), 4.24 (s, 4 H, NCH_2), 3.92 (d, J = 15.0 Hz, 2 H, NCH_2), 3.38 (s, 3 H, CH_3), 3.07 (br, 4 H, =CH), 2.49 (s, 6 H, CH_3), 2.35 (br, 4 H, =CCH_2), 1.55 (br, 4 H, =CCH_2). ^1H NMR (500 MHz, [D$_6$]acetone, 203 K): δ = 8.09 (t, J = 7.4 Hz, 1 H, py H_4), 7.97 (t, J = 7.4 Hz, 2 H, py H_4), 7.89 (d, J = 7.4 Hz, 2 H, py H_3), 7.63 (d, J = 7.4 Hz, 2 H, py H_5), 7.43 (d, J = 7.4 Hz, 2 H, py $H_{3,5}$), 4.78 (d, J = 17.0 Hz, 2 H, NCH_2), 4.72 (d, J = 17.0 Hz, 2 H, NCH_2), 4.52 (d, J = 15.0 Hz, 2 H, NCH_2), 4.26 (d, J = 13.0 Hz, 2 H, NCH_2), 4.19 (d, J = 13.0 Hz, 2 H, NCH_2), 3.88 (d, J = 15.0 Hz, 2 H, NCH_2), 3.42 (s, 3 H, CH_3), 3.15 (br, 2 H, =CH), 2.68 (br, 2 H, =CH), 2.59 (s, 6 H, CH_3), 2.30 (br, 2 H, =CCH_2), 1.97 (br, 2 H, =CCH_2), 1.51 (d, br, J = 8.1 Hz, 2 H, =CCH_2), 1.33 (d, br, J = 8.1 Hz, 2 H, =CCH_2). ^1H NOESY (chloride salt, 200 MHz, [D$_6$]acetone, 298 K, exchange cross-peaks): δ = (7.38⇄7.86, Py-$H_{3,5}$), (4.24⇄4.96, CH_2), (3.92⇄5.07), CH_2), (3.92⇄4.24, CH_2), (3.92⇄5.07, CH_2), (3.92⇄4.24, CH_2), (3.38⇄2.49, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 297 K): δ = 164 (2 C, py C_2), 160 (2 C, py C_6), 156 (2 C, py $C_{2,6}$), 139 (2 C, py C_4), 137 (1 C, py C_4), 124 (2 C, py C_3), 123 (2 C, py C_5), 122 (1 C, py $C_{3,5}$), 75.3 (br, 4 C, =CH), 64.5 (2 C, NCH_2), 63.7 (2 C, NCH_2), 63.0 (2 C, NCH_2), 47.7 (1 C, CH_3), 40.7 (2 C, NCH_3), 30.6 (4 C, =CCH_2), second =$CHCH_2$ signal obscured by acetone signal. FAB$^+$-MS (chloride salt): m/z = 403 [L^6 + H]$^+$, 425 [L^6 + Na]$^+$, 613 [L^{6}Rh(COD)]$^+$. IR (KBr): ṽ = 2931, 2884, 2866, 2844, 2796, 1602, 1584, 1572, 1455, 1427, 1159, 1116, 1094, 1040, 976, 877, 843, 800, 771, 558 cm^{-1}. $C_{32}H_{42}F_6N_6PRh$ (758.59): calcd. C 50.67, H 5.58, N 11.08; found C 49.84, H 6.05, N 10.38.

[L^{6}Rh(NBD)]PF$_6$: [Rh(NBD)Cl]$_2$ (57.2 mg, 0.12 mmol) was added to a solution of L^6 (100 mg, 0.25 mmol) and KPF_6 (184 mg, 1.0 mmol) in methanol (7.5 mL). The yellow reaction mixture was stirred for 1 h, after which the volume was concentrated to half its volume in vacuo. The product was precipitated by addition of water, filtered off, washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 140 mg (76%). ^1H NMR (500 MHz, [D$_6$]acetone, 273 K): δ = 7.94 (t, J = 7.6 Hz, 2 H, py H_4), 7.85 (t, J = 7.3 Hz, 1 H, py H_4), 7.79 (d, J = 7.6 Hz, 2 H, py H_3), 7.41 (d, J = 7.6 Hz, 2 H, py H_5), 7.38 (d, J = 7.3 Hz, 2 H, py $H_{3,5}$), 5.04 (d, J = 17.0 Hz, 2 H, NCH_2), 4.54 (d, J = 15.0 Hz, 2 H, NCH_2), 4.49 (d, J = 17.0 Hz, 2 H, NCH_2), 4.12 (s, 4 H, NCH_2), 3.95 (d, J = 15.0 Hz, 2 H, NCH_2), 3.58 (2 H, NBD CH_2), 3.08 (4 H, NBD = CH), 2.94 (s, 3 H, CH_3), 2.41 (s, 6 H, CH_3), 1.00 (2 H, NBD = CCH). ^1H NOESY (chloride salt, 200 MHz, [D$_6$]acetone, 298 K, exchange cross-peaks): δ = (7.52⇄7.70, py $H_{3,5}$), (7.36⇄7.81, py $H_{3,5}$ and py H_4), (4.48⇄5.08, NCH_2), (4.24⇄4.36, NCH_2), (4.14⇄5.08, NCH_2), (4.14⇄4.50, NCH_2), (2.46⇄2.95, CH_3). At this temperature all ligand signals are severely broadened. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 297 K): δ = 168 (2 C, py $C_{2,6}$), 163 (2 C, py $C_{2,6}$), 162 (2 C, py $C_{2,6}$), 144 (2 C, py C_4), 142 (1 C, py C_4), 2 × 128 (4 C, py $C_{3,5}$), 126 (2 C, py $C_{3,5}$), 70 (2 C, NCH_2), 67 (2 C, NCH_2), 67 (2 C, NCH_2), 63 (2 C, NBD CH_2), 53 (2 C, NBD =CH), 52 (1 C, CH_3), 46 (4 C, NBD =CCH), 43 (2 C, CH_3). FAB$^+$-MS: m/z = 597 [L^{6}Rh(NBD)]$^+$. IR (KBr): ṽ = 2932, 2917, 2863, 2841, 1604, 1588, 1574, 1462, 1450, 1427, 1160, 1096, 1051, 875, 842, 793, 777, 558 cm^{-1}. We did not obtain a satisfactory elemental analysis for this complex: $C_{31}H_{38}F_6N_6PRh$ (742.55): calcd. C 50.14, H 5.16, N 11.32; found C 46.99, H 4.74, N 10.38.

[L^{4}Ir(COD)]PF$_6$: [Ir(COD)Cl]$_2$ (25 mg, 0.037 mmol) was added to a solution of L^4 (20 mg, 0.075 mmol) in methanol. After addition of KPF_6 (14 mg), a yellow precipitate was collected by filtration. This was dissolved in dichloromethane, KCl was filtered off, and the solvent was evaporated in vacuo. Yield: 46 mg (85%). ^1H NMR (400 MHz, [D$_6$]acetone, 298 K): δ = 7.73 (t, J = 7.7 Hz, 2 H, py H_4), 7.39 (d, J = 7.6 Hz, 2 H, py H_3), 7.33 (d, J = 7.8 Hz, 2 H, py H_5), 6.03 (d, J = 14.0 Hz, 2 H, NCH_2), 4.87 (d, J = 16.8 Hz, 2 H, NCH_2), 4.61 (d, J = 16.9 Hz, 2 H, NCH_2), 4.48 (d, J = 14.1 Hz, 2 H, NCH_2), 3.84 (s, 3 H, CH_3), 3.79 (br, 2 H, =CH), 2.98 (br, 2 H, =CH), 2.75, (br, 2 H, =CCH_2), 2.39 (br, 2 H, =CCH_2), 2.29 (s, 3 H, CH_3), 1.76 (d, J = 7.9 Hz, 2 H, =CCH_2), 1.30 (d, J = 8.9 Hz, 2 H, =CCH_2). ^1H NOESY (400 MHz, [D$_6$]acetone, 298 K, exchange peaks): δ = (3.84⇄2.29, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 298 K): δ = 162 (2 C, py C_2), 160 (2 C, py C_6), 139 (2 C, py C_3), 127 (2 C, py C_4), 122 (2 C, py C_5), 70 (2 C, NCH_2), 66 (2 C, NCH_2), 65 (2 C, =CH), 55 (1 C, CH_3), 46 (2 C, =CH), 39 (1 C, CH_3), 35 (2 C, =CCH_2), 30 (2 C, =CCH_2). FAB$^+$-MS: m/z = 569 [L^{4}Ir(COD)]$^+$, 192 [Ir]$^+$. $C_{24}H_{32}F_6IrN_4P$ (713.73): calcd. C 40.39, H 4.52, N 7.85; found C 39.99, H 4.18, N 7.64.

[(L^{4}H)Ir(COD)](BF$_4$)$_2$: A solution of HBF_4 in ether (54 wt%, 3.86 mL) was added at 0 °C to a suspension of [L^{4}Ir(COD)]PF$_6$ (20 mg, 0.028 mmol) in methanol. The solvents were removed in vacuo. Treatment of the residue with methanol gave a yellow solution, from which a yellow solid [(L^{4}H)Ir(COD)](BF$_4$)$_2$ could be isolated by addition of 5 mL of diethyl ether. Overnight, the solution deposited further red crystals, suitable for X-ray diffraction. The complex is only poorly soluble in most solvents, while solutions in acetonitrile and methanol slowly decompose. We could therefore only partially interpret the ^1H NMR spectrum and did not obtain useful ^{13}C NMR spectroscopic data. ^1H NMR (200 MHz, CD_3OD, 298 K): δ = 7.73 (t, J = 7.7 Hz, 2 H, py H_4), 7.60 (d, J = 7.3 Hz, 2 H, py H_3), 7.36 (d, J = 7.5 Hz, 2 H, py H_5), 6.39 (d, J = 12.9 Hz, 2 H, NCH_2), 5.16 (d, J = 13.1 Hz, 2 H, NCH_2), 4.71 (d, J = 16.7 Hz, 2 H, NCH_2), 4.48 (d, J = 16.9 Hz, 2 H, NCH_2), 3.70 (s, 3 H, CH_3), 2.70 (br, 2 H, =CH), 2.37 (br, 2 H, =CCH_2), 2.04 (br, 2 H, =CCH_2), 1.74 (br, 2 H, =CCH_2), 1.28 (br, 2 H, =CCH_2).

[L^{4}Ir(C$_8$H$_{11}$O)](PF$_6$)$_2$: H(OEt$_2$)$_2^+$B(Ar^F)$_4^-$ (28.4 mg, 0.028 mmol) was added to a solution of [L^{4}Ir(COD)]PF$_6$ (20 mg, 0.028 mmol) in acetonitrile. After 5 min, aqueous hydrogen peroxide (1%, 0.08 mL) was added, after which the mixture was stirred vigorously for 15 min. Removal of the solvent in vacuo gave a yellow solid, which could be dissolved in methanol. Addition of KPF_6 (14 mg) yielded a yellow solid, which could be "crystallised" as droplets from acetonitrile by slow diffusion of diethyl ether into the solution. Yield: 22 mg (90%). When the reaction was attempted with only 0.5 equiv. of H(OEt$_2$)$_2^+$B(Ar^F)$_4^-$, a 1:1 mixture of [L^{4}Ir(COD)]PF$_6$ and

$[L^4Ir(C_8H_{11}O)](PF_6)_2$ was isolated. $[L^4Ir(C_8H_{11}O)](PF_6)_2$ is an air-stable, yellow solid. ^1H NMR (600 MHz, [D$_6$]acetone, 298 K): δ = 8.15 (t, J = 8.16 Hz, 1 H, py H_4), 8.02 (t, J = 7.7 Hz, 1 H, py H_4), 7.70 (d, J = 8.1 Hz, 1 H, py H_3), 7.67 (d, J = 7.4 Hz, 1 H, py H_3), 7.65 (d, J = 7.8 Hz, 1 H, py H_5), 7.61 (d, J = 7.4 Hz, 1 H, py H_5), 6.94 (br, 1 H, =C*H*), 6.75 (br, 1 H, =C*H*), 5.47 (d, J = 16.7 Hz, 1 H, NCH_2), 5.31 (d, J = 16.3 Hz, 2 H, NCH_2), 4.79 (d, J = 16.8 Hz, 1 H, NCH_2), 4.75 (d, J = 16.7 Hz, 1 H, NCH_2), 4.64 (d, J = 16.3 Hz, 1 H, NCH_2), 4.62 (d, J = 15.9 Hz, 1 H, NCH_2), 4.31 (d, J = 16.3 Hz, 1 H, NCH_2), 3.76 (br, 1 H, COD CH_2), 3.51 (s, 3 H, CH_3), 3.22 (br, 1 H, COD CH_2), 3.14 (s, 3 H, CH_3), 3.12 (br, 1 H, COD CH_2), 2.99 (br, 1 H, COD CH_2), 2.67 (br, 1 H, COD CH_2), 2.53 (br, 1 H, COD CH_2), 2.38 (br, 1 H, COD CH_2), 1.83 (dd, J_1 = 9.7 Hz, J_2 = 15.9 Hz, 1 H, Ir-C*H*). One COD CH_2 proton signal is probably obscured by a solvent signal. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 298 K): δ = 220.8 (1 C, *C*=O), 157.5 (1 C, py C_2), 157.0 (1 C, py C_2), 156.9 (1 C, py C_6), 156.5 (1 C, py C_6), 142.5 (1 C, py C_4), 142.2 (1 C, py C_4), 123.2 (1 C, py C_3), 123.1 (1 C, py C_3), 123.0 (1 C, py C_5), 122.7 (1 C, py C_5), 100.4 (1 C, =*C*H), 88.2 (1 C, =*C*H), 80.4 (1 C, N*C*H$_2$), 78.9 (1 C, N*C*H$_2$), 77.9 (1 C, N*C*H$_2$), 76.4 (1C, N*C*H$_2$), 57.1 (1 C, *C*H$_3$), 53.5 (1 C, *C*H$_3$), 38.1 (1 C, =C*C*H$_2$), 36.1 (1 C, O=C*C*H$_2$), 28.7 (1 C, =C*C*H$_2$), 28.6 (1 C, =C*C*H$_2$), 25.3 (1 C, Ir-*C*). ^1H NOESY (600 MHz, [D$_6$]acetone, 298 K, cross peaks): δ = (6.94/5.31, =C*H*/CH_2), (6.75/5.47, =C*H*/CH_2), (6.94/3.51, =C*H*/CH_3), (6.75/3.14 (=C*H*/CH_3). MALDI-TOF-MS: m/z = 583 $[L^4Ir(C_8H_{11}O)]^+$, 556 $[L^4Ir(C_8H_{11}O) - HCN]^+$, 493 [?]$^+$, 459 $[L^4Ir]^+$, 269 $[L^4H]^+$. $C_{24}H_{31}F_{12}IrN_4OP_2$ (873.68): calcd. C 32.99, H 3.58, N 6.41; found C 32.80, H 3.63, N 6.38. X-ray quality crystals were obtained by crystallization from acetone, and were found to contain one molecule of diacetone alcohol of crystallization (see below).

X-ray Structure Determinations: Single crystals were mounted in air on glass fibres. Intensity data were collected at room temperature with an Enraf−Nonius CAD4 single-crystal diffractometer. Unit-cell dimensions were determined from the angular setting of a limited number of reference reflections. Intensity data were corrected for Lorentz and polarization effects, and for absorption using a semiempirical ψ-scan correction.[23] Structures were solved by the DIRDIF[24] program system, using the PATTY[25] program to locate the heavy atom (Rh or Ir), and refined with standard methods (refinement against F^2 of all reflections) with SHELXL97.[26] All

Table 2. Details of X-ray structure determinations

Compound	$[L^4Rh(COD)]PF_6$	$[L^6Rh(COD)]PF_6$	$[L^6Rh(NBD)]PF_6 \cdot C_3H_6O$	$[(L^4H)Ir](BF_4)_2$	$[L^4Ir(C_8H_{11}O)](PF_6)_2 \cdot C_6H_{12}O_2$
Crystal colour	transparent yellow-brown	transparent brown-yellow	yellow, degraded, cracked	transparent dark red	transparent yellow
Crystal shape	fairly regular thick platelet	fairly regular platelet	regular fragment	rather irregular fragment	irregular fragment
Crystal size [mm]	0.31 × 0.26 × 0.11	0.42 × 0.39 × 0.08	0.44 × 0.40 × 0.23	0.39 × 0.33 × 0.21	0.39 × 0.36 × 0.31
Empirical formula	$C_{24}H_{32}F_6N_4PRh$	$C_{32}H_{42}F_6N_6PRh$	$C_{34}H_{44}F_6N_6OPRh$	$C_{24}H_{33}B_2F_8IrN_4$	$C_{30}H_{43}F_{12}IrN_4O_3P_2$
Molecular mass	624.42	758.60	800.63	743.36	989.82
Temperature [K]	293(2)	208(2)	208(2)	293(2)	293(2)
Radiation (graphite mon.)	Cu-K_α	Cu-K_α	Cu-K_α	Cu-K_α	Mo-K_α
Wavelength [Å]	1.54184	1.54184	1.54184	1.54184	0.71073
Crystal system, space group	monoclinic, *P*21/*c*	orthorhombic, *Pbca*	triclinic, *P*-1	orthorhombic, *Pnma*	monoclinic, *C*2/*c*
No. of unit-cell reflections,	12,	25,	25,	21,	25,
θ range [°]	22.435−45.250	40.367−46.985	34.259−39.151	40.232−46.897	18.474−20.669
a [Å]	8.828(11)	18.9991(9)	11.1345(5)	10.5427(11)	21.871(3)
b [Å]	15.163(3)	15.1936(7)	13.3241(10)	13.7308(7)	13.847(5)
c [Å]	18.949(2)	22.3517(8)	13.4933(7)	17.9889(5)	24.995(3)
α [°]	90	90	96.372(4)	90	90
β [°]	92.030(19)	90	109.201(5)	90	104.026(11)
γ [°]	90	90	103.779(10)	90	90
V [Å^3]	2535(3)	6452.2(5)	1796.51(18)	2604.1(3)	7344(3)
Z, calcd. density [Mg·m^{-3}]	4, 1.636	8, 1.562	2, 1.480	4, 1.896	8, 1.791
Abs. coefficient [mm^{-1}]	6.633	5.345	4.853	10.651	3.822
Scan	θ/2θ	θ/2θ	θ/2θ	θ/2θ	ω
F(000)	1272	3120	824	1456	3920
θ range for data collection [°]	3.73−70.22	3.96−69.99	3.49−64.97	4.05−69.89	3.06−26.31
Index ranges	$-10 \le h \le 0$ $0 \le k \le 18$ $-23 \le l \le 23$	$0 \le h \le 23$ $0 \le k \le 18$ $0 \le l \le 27$	$-12 \le h \le 13$ $-15 \le k \le 15$ $-15 \le l \le 0$	$-12 \le h \le 0$ $-15 \le k \le 0$ $0 \le l \le 21$	$-27 \le h \le 0$ $0 \le k \le 17$ $-30 \le l \le 31$
Refl. collected/unique (R_{int})	5137/4810 (0.0289)	6110/6110	6382/6091 (0.0138)	2573/2573	7608/7408 (0.0273)
Refl. observed [$I_o > 2\sigma(I_o)$]	3377	5225	5962	2200	5072
Abs. corr.	semiemp. ψ-scan	semiemp. ψ-scan	semiemp. ψ-scan	semiemp. ψ-scan + DIFABS	semiemp. ψ-scan
Range of rel. transm. factors	2.069 and 0.852	2.648 and 0.786	1.037 and 0.968	1.369 and 0.805	1.100 and 0.936
Data/restraints/parameters	4810/0/343	6110/0/418	6091/24/598	2573/2/189	7408/0/475
Goodness-of-fit on F^2	1.034	1.051	1.059	1.062	1.041
SHELXL-97 wt parameters	0.0912, 6.8763	0.1016, 16.9184	0.070, 4.396	0.0562, 9.6517	
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0601, 0.1472	0.0599, 0.1626	0.0447, 0.1207	0.0411, 0.0985	0.0588, 0.1406
$R1$, $wR2$ (all data)	0.0942, 0.1713	0.0683, 0.1713	0.0453, 0.1213	0.0515, 0.1036	0.0974, 0.1607
Diff. peak and hole [e·Å^{-3}]	1.813 and −0.981	1.422 and −1.418	1.690 and −0.970	1.294 and −1.229	2.600 and −1.155

non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically in riding mode, unless otherwise noted. Geometrical calculations (PLATON[27]) revealed neither unusual geometric features, nor unusual short intermolecular contacts, no higher symmetry and no (further) solvent-accessible areas. Details of the data collection and structure determinations are collected in Table 2. − **[L^{4}Rh(COD)]PF$_6$:** Hydrogen atoms attached to C11, C12, C21, and C22 were freely refined. − **[L^{6}Rh(NBD)]PF$_6$·C$_3$H$_6$O:** The hydrogen atoms of the acetone methyl groups were refined as rigid rotors with idealized sp^3 hybridization and a C−H bond length of 0.97 Å to match maximum electron density in a difference Fourier map. All other hydrogen atoms were initially placed at calculated positions and were subsequently freely refined. − **[(L^{4}H)Ir(COD)](BF$_4$)$_2$:** The normal least-squares refinement procedure failed to give acceptable anisotropic displacement parameters for a number of atoms. Refinement in space group *Pna*21, although possible and resulting in an even lower *R* value (0.1118 vs. 0.1161 isotropic, 0.0607 vs. 0.0638 anisotropic), produced even worse displacement parameters. Because the irregular crystal shape prevented adequate analytic absorption correction, the DIFABS procedure[28] was applied after all atoms, including hydrogen atoms, had been refined isotropically in *Pnma*. After this correction, refinement in *Pnma* lowered the isotropic *R* value from 0.1161 to 0.0530, and the anisotropic *R* value from 0.0638 to 0.0410, with perfectly acceptable anisotropic displacement parameters. Further refinement in *Pna*21, however, again gave nonpositive definite values for most atoms. Besides this, there is no significant change/improvement in the geometry in those parts of the structure (esp. the COD moiety) that are possibly constrained most by the imposed symmetry. The statistical distribution of *E* values favours the centrosymmetric space group *Pnma*. However, all the structures containing cyclooctadiene that we have solved so far showed a twist in the COD moiety, through which an eclipsed conformation of the CH_2CH_2 groups is avoided. The mirror symmetry imposed on the COD moiety in space group *Pnma* does not conform with this convincing observation, and the refinement in *Pna*21 clearly shows the expected torsion in the COD moiety. Therefore, we believe that the average structure shows an overall centrosymmetric arrangement in which mainly the COD moiety is disordered to a certain extent, although there will also be some effect on the remainder of the structure. Unfortunately, if this is the case then the deviations from a centrosymmetric structure are not large enough to allow for a disorder refinement. The bond lengths in the COD fragment should be treated with caution. − **[L^{4}Ir(C$_8$H$_{11}$O)](PF$_6$)$_2$·C$_6$H$_{12}$O$_2$:** The diacetone alcohol molecule of crystallization shows large displacement parameters and is probably disordered. The assignments of O77 and O78 as oxygen atoms is based on bond lengths only, and that of O77 is not certain. The hydrogen bond involving H77 must therefore be regarded as tentative. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-166291−166295. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: Fitted rate constants for [L^{4}Rh(COD)]$^+$, [L^{6}Rh(COD)]$^+$, and [L^{4}Ir(COD)]$^+$ and the Arrhenius and Eyring plots used to derive activation parameters.

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