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Ligand redistribution reactions of some organometallic rhodium and iridium complexes

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Abstract

Ligand redistribution reactions of some organometallic rhodium and iridium complexes have been investigated and their possible reaction pathways have been discussed.

Ligand redistribution reactions in transition-metal organometallic systems play a role of paramount importance in catalytic and stoichiometric transformations [1]. Although Vaska's type complexes *trans*-M(X)(CO)$(PR_3)_2$ (M = Ir, Rh) have been extensively studied in oxidative addition reactions in organometallic chemistry, studies of intermolecular redistribution of ligands involving these types of complexes are relatively rare [2]. In continuation of our studies on the reactivity of the newly prepared rhodium and iridium triflate complexes *trans*-M(OTf)(CO)$(PR_3)_2$ (M = Ir, Rh) [3–6], we have had occasion to investigate the reactions in which a ligand redistribution occurs between two metal centers. Here, we report on this intermolecular transfer phenomena which results from the following reactions.

Results and discussion

Reaction of trans-*M(OTf)(CO)*$(PPh_3)_2$ *with* trans-*M(Cl)(CO)*$(PPh_3)_2$ *(M = Ir, Rh)*

Reaction of *trans*-Rh(OTf)(CO)$(PPh_3)_2$ (**2**) [7] and 1.0 equiv. of *trans*-Ir(Cl)(CO)$(PPh_3)_2$ (**3**) [8] in benzene-d_6 was followed by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. Four $^{31}P\{^1H\}$ NMR signals are observed within 15 min at (relative peak intensities) 29.88 ppm (6.5%), 28.50 ppm (68.5%), 27.76 ppm (10.6%), and 24.87 ppm (100%), corresponding to complexes *trans*-Rh(Cl)(CO)$(PPh_3)_2$ (**4**) [9], *trans*-Rh(OTf)(CO)$(PPh_3)_2$ (**2**), *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**1**) [10], and *trans*-Ir(Cl)(CO)$(PPh_3)_2$ (**3**), respectively. This result indicates that chloride and triflate ligand exchange between Rh and Ir metal centers has occurred. These product ratios remain largely unchanged over the course of 24 h at room tempera-

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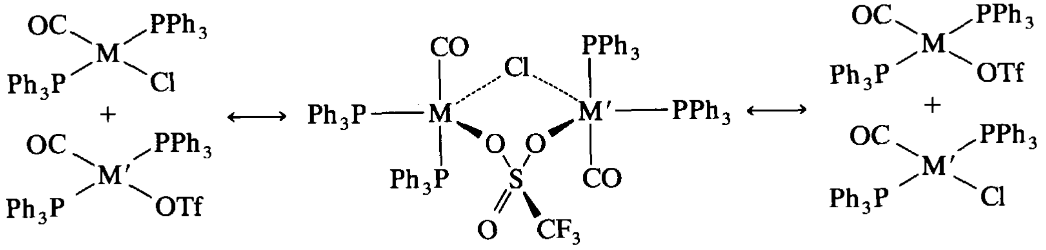
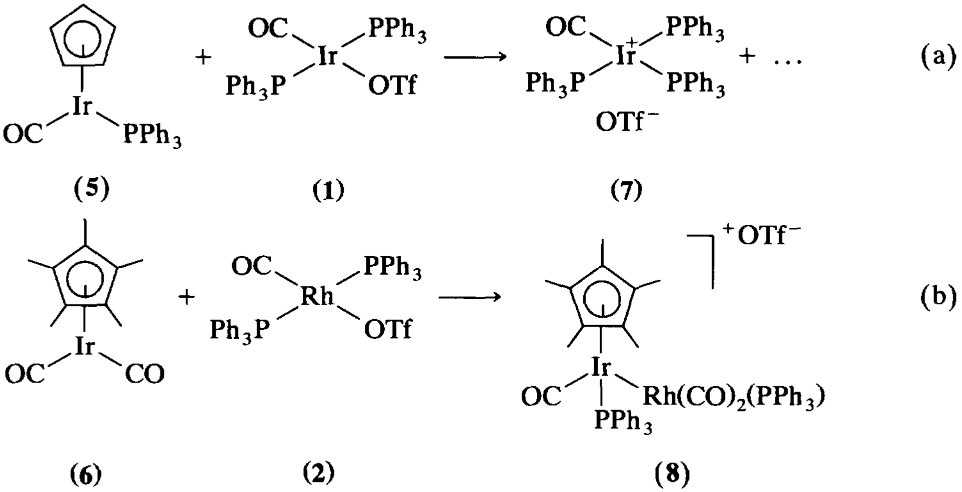


Scheme 1.



Scheme 2.

ture. Likewise, the same products and similar peak intensities are observed by $^{31}P\{^1H\}$ NMR monitoring when equimolar quantities of *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (1) and *trans*-Rh(Cl)(CO)$(PPh_3)_2$ (4) are combined in benzene-d_6. No intermediate was detected in either of these reactions.

The intermolecular redistribution of chloride and triflate ligands might take place through an oxidative addition-reductive elimination sequence via a metal–metal bonded, heterobimetallic intermediate $(PPh_3)_2$(CO)M′–M(OTf)(Cl)(CO)-$(PPh_3)_2$ (M′ = Rh, M = Ir; M′ = Ir, M = Rh). Alternatively, it may occur by an associative pathway for halide exchange which has been discussed by others involving Vaska's type compounds forming a cyclic, doubly five-coordinatively bridged intermediate in the intermolecular transfer (Scheme 1) [2b].

Reaction of trans-*M(OTf)(CO)(PPh$_3$)$_2$ (M = Ir, Rh) with (η^5-C$_5$R$_5$)Ir(CO)L (R = H, L = PPh$_3$; R = Me, L = CO)*

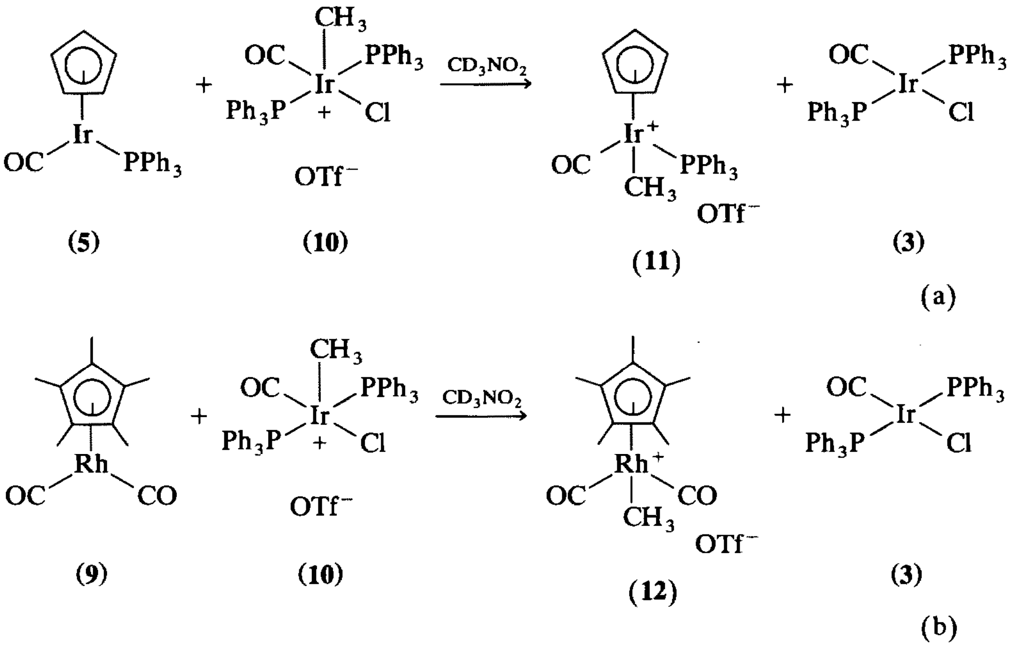
trans-Ir(OTf)(CO)$(PPh_3)_2$ (1) and an equimolar quantity of $(\eta^5\text{-}C_5H_5)$Ir(CO)(PPh_3) (5) [11] were combined in CH_2Cl_2 at room temperature (Scheme 2(a)). The solution instantly acquired an orange color upon mixing. The $^{31}P\{^1H\}$ NMR spectrum of the solution shows a number of low intensity signals in addition to an intense doublet and an intense triplet resonance in a 2:1 ratio appearing at 15.43 ppm (d, J(P–P) = 29.3 Hz) and 17.96 ppm (t, J(P–P) = 29.3 Hz), respectively. Analysis of this spectroscopic data indicates that the reaction gave $[Ir(CO)(PPh_3)_3]^+$ $[OTf]^-$ (7) as the major product. The doublet at 15.43 ppm is assigned to the two mutually trans PPh_3 ligands, and the triplet at 17.96 ppm is attributed to the other PPh_3 ligand trans to the carbonyl group. Our inability to identify any organometallic products other than 7 leaves the fate of the $(\eta^5\text{-}C_5H_5)$Ir(CO) moiety unresolved. The identity of 7 was confirmed by an independent, $^{31}P\{^1H\}$ NMR-monitored synthesis from *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (1) and PPh_3 (1.0 equiv., $CDCl_3$, room temperature).

Next, the reaction of *trans*-Rh(OTf)(CO)(PPh$_3$)$_2$ (**2**) and (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (**6**) [12] in CD$_3$NO$_2$ was monitored by ^{31}P{^{1}H} NMR spectroscopy at room temperature (Scheme 2(b)). The ^{31}P{^{1}H} NMR spectrum shows that the reactants are consumed within 4 h giving rise to two major resonances in a 1 : 1 ratio at 33.49 and 3.33 ppm demonstrating nonequivalent phosphorous environments. The resonance centered at 33.49 ppm (dd, J(P–Rh) = 137.8 Hz, J(P–P) = 6.9 Hz) appearing as a doublet of doublets with P–Rh and P–P couplings is assigned to the triphenylphosphine ligand attached to the Rh metal center, while the resonance at 3.33 ppm (d, J(P–P) = 6.9 Hz) which is observed as a doublet due to P–P coupling arises from the remaining triphenylphosphine group bonded to the Ir atom. In addition, these observations suggest that a ligand exchange (CO for PPh$_3$) has occurred between the Rh and Ir metal centers. The mutual coupling between two different triphenylphosphine ligands also implies the presence of a metal–metal bond in the product complex. Furthermore, the corresponding ^{1}H NMR spectrum shows the C$_5$Me$_5$ proton resonance at δ 1.98 as a doublet with phosphorous coupling (d, J(H–P) = 2.1 Hz) in addition to the aromatic protons appearing at δ 7.80–7.15. Thus, on the basis of the spectroscopic data, the product is tentatively assigned as heterobimetallic complex [(η^5-C$_5$Me$_5$)(CO)(PPh$_3$)Ir–Rh(CO)$_2$(PPh$_3$)]$^+$[OTf]$^-$ (**8**) (Scheme 2(b)). However, numerous attempts at isolating the pure, solid product **8** from the reaction mixture were not successful.

In view of the literature precedent [13], the relative lability of the triflate ligand among the ligands in complexes used, and comparison of the results in Scheme 2(a), (b), it is highly probable that reaction of **1** with (η^5-C$_5$H$_5$)Ir(CO)(PPh$_3$) (**5**) proceeds via initial attack of the metal nucleophile **5** upon the metal center of the triflate complex. This generates the metal–metal bonded homobimetallic [(η^5-C$_5$H$_5$)(CO)(PPh$_3$)Ir–Ir(CO)(PPh$_3$)$_2$]$^+$[OTf]$^-$ intermediate of Scheme 2(a). The resulting intermediate could at some point rearrange to give unidentifiable species and tris(triphenylphosphine) complex. In addition, the heterobimetallic product **8** observed in Scheme 2(b) provides further support for this postulated intermediate since the presence of a metal–metal bond is clearly indicated by P–P coupling in the ^{31}P{^{1}H} NMR spectrum.

Reaction of Ir(OTf)(CH$_3$)(Cl)(CO)(PPh$_3$)$_2$ with (η^5-C$_5$R$_5$)M(CO)L (R = H, L = PPh$_3$, M = Ir; R = Me, L = CO, M = Rh)

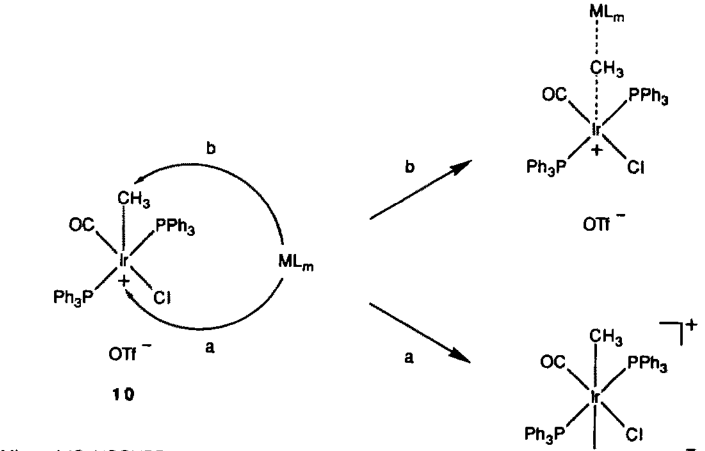
When (η^5-C$_5$H$_5$)Ir(CO)(PPh$_3$) (**5**) and an equimolar amount of Ir(OTf)(CH$_3$)(Cl)(CO)(PPh$_3$)$_2$ (**10**) [14] were combined and shaken (Scheme 3(a)) with CD$_3$NO$_2$ in a 5-mm NMR tube at room temperature, the reaction led cleanly and rapidly to the formation of known *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ (**3**) as a bright yellow microcrystalline precipitate, which was separated from the supernatant and characterized by IR and ^{31}P{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum of the supernatant shows a single resonance at 2.47 ppm, characteristic of octahedral iridium complexes. The corresponding ^{1}H NMR spectrum indicates the clean formation of [(η^5-C$_5$H$_5$)Ir-(CH$_3$)(CO)(PPh$_3$)]$^+$[OTf]$^-$ (**11**) [11] as evidenced by the observed signals (CD$_3$NO$_2$): δ 7.70–7.43 (m, PPh$_3$); 5.91 (d, J(H–P) = 1.2 Hz, C$_5$H$_5$); 1.14 (d, J(H–P) = 5.1 Hz, Ir–CH$_3$). Likewise, reaction of (η^5-C$_5$Me$_5$)Rh(CO)$_2$ (**9**) [15] with Ir(OTf)(CH$_3$)(Cl)(CO)(PPh$_3$)$_2$ (**10**) (Scheme 3(b)) in CD$_3$NO$_2$ at room temperature leads cleanly and rapidly to the formation of *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ (**3**) and [(η^5-C$_5$Me$_5$)Rh(CH$_3$)(CO)$_2$]$^+$[OTf]$^-$ (**12**). Complex **12**, as analyzed *in situ*,



Scheme 3.

displays the following resonances: ^1H NMR (CD_3NO_2): δ 2.12 (d, J(H–Rh) = 0.5 Hz, C_5Me_5); 1.23 (d, J(H–Rh) = 2.0 Hz, Rh–CH_3). Both reactions indicate that the transfer of a methyl group has occurred.

The reaction of metal nucleophile **5** or **9** with $Ir(OTf)(CH_3)(Cl)(CO)(PPh_3)_2$ (**10**) may be visualized as proceeding via two pathways: (a) and (b) as shown in Scheme 4. Since complex **10** acts as a 1 : 1 electrolyte in polar solvents [14] such as nitromethane, the positive metal center would be susceptible to attack by metal



ML_m = $Ir(Cp)(CO)(PPh_3)$ (**5**), $Rh(Cp^*)(CO)_2$ (**9**)

Scheme 4.

nucleophiles. This would give rise to metal–metal bonded intermediates, which could undergo a methyl group migration to give ligand exchange products (pathway (a)). Alternatively, the metal nucleophiles may approach the substrate from the less hindered site and attack directly at the methyl carbon resulting in the formation of the same products (pathway (b)).

In summary, the reaction of *trans*-$M(OTf)(CO)(PPh_3)_2$ (M = Ir, **1**; Rh, **2**) with *trans*-$M(Cl)(CO)(PPh_3)_2$ (M = Rh, **4**; Ir, **3**) demonstrates that triflate and chloride ligands can be transferred between two metal centers affording ligand exchange products. The labile triflate complex **1** also undergoes a facile reaction with $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$ (**5**) yielding ligand exchange products, one of which is identified as $[Ir(CO)(PPh_3)_3]^+[OTf]^-$ (**7**). This reaction may be interpreted as arising via a metal–metal bonded intermediate. Spectroscopic evidence for the existence of this type of intermediate has been obtained in the reaction between **2** and $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ (**6**). The transfer of a methyl group from iridium to iridium and from iridium to rhodium has also been observed in the reactions of $Ir(OTf)(CH_3)(Cl)(CO)(PPh_3)_2$ (**10**) with $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$ (**5**) and $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ (**9**), respectively.

Experimental section

General methods

General procedures and purification methods for solvents and reagents employed in this study have been previously described [3–6].

Reaction of trans-*Rh(OTf)(CO)(PPh$_3$)$_2$ (2) with* trans-*Ir(Cl)(CO)(PPh$_3$)$_2$ (3)*

A 5-mm NMR tube was charged with **2** (0.011 g, 0.013 mmol) and **3** (0.010 g, 0.013 mmol) and was capped with a rubber septum. A needle, connected to a vacuum line, was inserted through the rubber septum. The NMR tube was degassed under vacuum and then was saturated with nitrogen. Benzene-d_6 (1.2 mL) was injected by syringe. The NMR tube was removed from the vacuum line and was shaken vigorously to effect dissolution. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Four $^{31}P\{^1H\}$ NMR signals were observed within 15 min at (relative peak intensities) 29.88 ppm (6.5%), 28.50 ppm (68.5%), 27.76 ppm (10.6%), and 24.87 ppm (100%), corresponding to complexes *trans*-$Rh(Cl)(CO)(PPh_3)_2$ (**4**), *trans*-$Rh(OTf)(CO)(PPh_3)_2$ (**2**), *trans*-$Ir(OTf)(CO)(PPh_3)_2$ (**1**), and *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (**3**), respectively. These product ratios remained largely unchanged over the course of 24 h at room temperature.

Reaction of trans-Ir(OTf)(CO)(PPh$_3$)$_2$ (1) with trans-*Rh(Cl)(CO)(PPh$_3$)$_2$ (4)*

The sample was prepared in a 5-mm NMR tube from **1** (0.013 g, 0.015 mmol), **4** (0.010 g, 0.015 mmol), and benzene-d_6 (1.2 mL) by a procedure identical to that given above. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Four $^{31}P\{^1H\}$ NMR signals were observed within 15 min at (relative peak intensities) 29.88 ppm (8.3%), 28.50 ppm (71.8%), 27.76 ppm (5.3%) and 24.87 ppm (100%), corresponding to complexes *trans*-$Rh(Cl)(CO)(PPh_3)_2$ (**4**), *trans*-$Rh(OTf)(CO)(PPh_3)_2$ (**2**), *trans*-$Ir(OTf)(CO)(PPh_3)_2$ (**1**) and *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (**3**), respectively. These product ratios remained largely unchanged over the course of 24 h at room temperature.

Reaction of trans-*Ir(OTf)(CO)(PPh$_3$)$_2$ (1) with (η^5-C$_5$H$_5$)Ir(CO)(PPh$_3$) (5)*

The sample was prepared in a 5-mm NMR tube from **1** (0.016 g, 0.018 mmol), **5** (0.010 g, 0.018 mmol), and CH_2Cl_2 (0.7 mL) by a procedure identical to that given above. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed the major product to be identical with an authentic sample of $[Ir(CO)(PPh_3)_3]^+[OTf]^-$ (**7**).

Reaction of trans-*Rh(OTf)(CO)(PPh$_3$)$_2$ (2) with (η^5-C$_5$Me$_5$)Ir(CO)$_2$ (6)*

The sample was prepared in a 5-mm NMR tube from **2** (0.020 g, 0.025 mmol), **6** (0.010 g, 0.026 mmol), and CD_3NO_2 (0.7 mL) by a procedure identical to that given above. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Data on product $[(\eta^5\text{-}C_5Me_5)(CO)(PPh_3)Ir\text{–}Rh(CO)_2(PPh_3)]^+[OTf]^-$ (**8**): ^1H NMR (CD_3NO_2): δ 7.80–7.15 (m, 2 PPh_3); 1.98 (d, J(H–P) = 2.1 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_3NO_2): 33.49 (dd, J(P–Rh) = 137.8 Hz, J(P–P) = 6.9 Hz, Rh–PPh_3); 3.33 (d, J(P–P) = 6.9 Hz, Ir–PPh_3) ppm.

Reaction of Ir(CH$_3$)(OTf)(CO)(Cl)(PPh$_3$)$_2$ (10) with (η^5-C$_5$H$_5$)Ir(CO)(PPh$_3$) (5)

The sample was prepared in a 5-mm NMR tube from **10** (0.021 g, 0.022 mmol), **5** (0.012 g, 0.022 mmol), and CD_3NO_2 (0.7 mL) by a procedure identical to that given above. The reaction led cleanly and rapidly to the formation of known *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (**3**) as a bright yellow microcrystalline precipitate, which was separated from the supernatant and characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of the supernatant showed a single resonance at 2.47 ppm, characteristic of octahedral iridium complexes. The corresponding ^1H NMR spectrum indicated the clean formation of $[(\eta^5\text{-}C_5H_5)Ir(CH_3)(CO)(PPh_3)]^+[OTf]^-$ (**11**) as evidenced by the observed signals (CD_3NO_2): δ 7.70–7.43 (m, PPh_3); 5.91 (d, J(H–P) = 1.2 Hz, C_5H_5); 1.14 (d, J(H–P) = 5.1 Hz, Ir–CH_3).

Reaction of Ir(CH$_3$)(OTf)(CO)(Cl)(PPh$_3$)$_2$ (10) with (η^5-C$_5$Me$_5$)Rh(CO)$_2$ (9)

The sample was prepared in a 5-mm NMR tube from **10** (0.029 g, 0.031 mmol), **9** (0.009 g, 0.031 mmol) and CD_3NO_2 (0.7 mL) by a procedure identical to that given above. The reaction led cleanly and rapidly to the formation of known *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (**3**) as a bright yellow microcrystalline precipitate, which was separated from the supernatant and characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of the supernatant indicated the clean formation of $[(\eta^5\text{-}C_5Me_5)Rh(CH_3)(CO)_2]^+[OTf]^-$ (**12**) as evidenced by the observed signals (CD_3NO_2): δ 2.12 (d, J(H–Rh) = 0.5 Hz, C_5Me_5); 1.23 (d, J(H–Rh) = 2.0 Hz, Rh–CH_3).

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