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Cycloheptatrienyl bridged heterobimetallic complexes: synthesis and reactivity of $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$

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Abstract

The synthesis and spectroscopic properties of the cycloheptatrienyl bridged ruthenium-iridium complex $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$ (**2**) is described. **2** undergoes phosphine substitution reactions with PPh_3 at Ir and with DPPM at both metal centers. Within the series of complexes $(\mu\text{-}C_7H_7)M(CO)_3M'(CO)PPh_3$ (M = Fe, Ru; M′ = Rh, Ir) the rate of intermetallic carbonyl exchange increases upon descending a triad for M and M′.

Introduction

The unique chemical reactivity potentially accessible upon introducing two different transition metals into a molecule has given rise to the synthesis and study of a wide variety of heterobimetallic transition metal complexes [1].

We have previously described the preparation and chemical properties of cycloheptatrienyl bridged heterobimetallic carbonyl complexes of FeRh [2], RuRh [3], and FeIr [4]. It has been suggested that the variable bonding capability, and the incipient coordinative unsaturation of the cycloheptatrienyl ring are responsible for facile CO substitution and carbonyl scrambling processes in these complexes. In continuation of these investigations we now describe the preparation and characterization of some cycloheptatrienyl bridged ruthenium-iridium complexes.

Results and discussion

Addition of $K(C_7H_7)Ru(CO)_3$ to $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ in THF gives $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(COD)$ (**1**) in 23% yield (eq. 1). Complex **1** is isolated as yellow, air stable crystals, freely soluble in common organic solvents. The IR spectrum displays a three band pattern consistent with three carbonyl groups occupying terminal positions on Ru. Whilst the yield of **1** is poor, it is similar to that observed (30%) for the analogous RuRh complex prepared under similar conditions [5]. On reaction

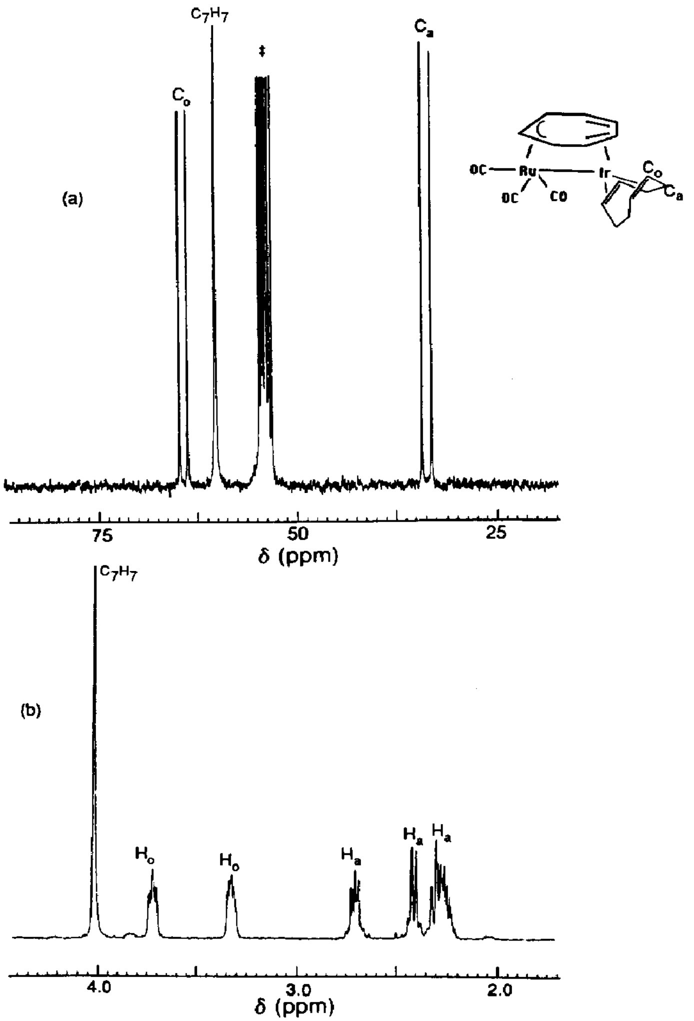


Fig. 1. ^{13}C (a) and ^{1}H (b) NMR spectra of **1** in the C_7H_7 and COD regions.

with CO, **1** is quantitatively converted to $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$ (**2**) at 100 °C over 2 h (eq. 2). Complex **2** is a yellow-orange, air stable and thermally robust solid, also soluble in most organic solvents. The IR spectrum shows five peaks in the terminal carbonyl region as has been previously observed for the related FeRh, FeIr, and RuRh complexes.

$$K(C_7H_7)Ru(CO)_3 + \tfrac{1}{2}[Ir(COD)Cl]_2 \xrightarrow[RT]{THF} \underset{(\mathbf{1})}{(\mu\text{-}C_7H_7)Ru(CO)_3Ir(COD)} \quad (1)$$

(COD = 1,5 cyclooctadiene)

$$\underset{(\mathbf{1})}{(\mu\text{-}C_7H_7)Ru(CO)_3Ir(COD)} + CO \xrightarrow[100\,^{\circ}C,\ 2h]{octane} \underset{(\mathbf{2})}{(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2} \quad (2)$$

As expected the ^{1}H and ^{13}C NMR data for **1** and **2** give evidence for rapid ring whizzing of the cycloheptatrienyl ligand at ambient temperature. However as can be seen in Fig. 1, rotation of the COD ligand in **1** is not observed, there being two sharp resonances for the olefinic hydrogens and carbons in the ^{1}H and ^{13}C NMR spectra respectively. A similar observation was made in the corresponding FeIr compound [4], but in the analagous RuRh complex [5] rotation of the COD ligand occurs as evidenced by the single olefinic resonance in the room temperature ^1H NMR spectrum. This reflects the well known decrease in metal to ligand bond strength upon ascending a transition metal triad [6]. The observation that complex **2** requires temperatures of 70 °C to give complete enrichment with ^{13}CO is also consistent with this trend.

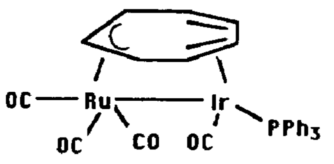
Interestingly, the variable temperature ^1H NMR spectra of **1** and **2** indicate freezing out of the rotation of the μ-C_7H_7 ligand. The low temperature limiting spectra is approached at $-100\,°C$ for both complexes. We will comment more fully on this and complementary results in related Os complexes in a forthcoming publication [7].

In their ^{13}C NMR spectra both complexes **1** and **2** display a sharp singlet for the three CO ligands on Ru due to rapid scrambling of the CO groups on one metal centre. Intermetallic CO exchange is not observed in **2** at ambient temperature; there being two sharp resonances at δ 196 ppm (CO_{Ru}) and δ 175 ppm (CO_{Ir}), easily distinguishable on the basis of their chemical shifts [8]. These signals remain sharp until 70 °C when slight broadening is noticed. Coalescence is not reached at 100 °C at which point slight decomposition of the sample occurs. Intermetallic CO scrambling was also not observed even at elevated temperatures for the analogous FeRh, FeIr, and RuRh pentacarbonyl complexes.

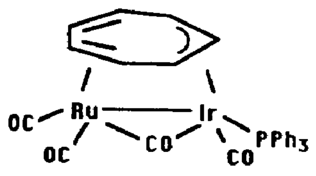
Although the carbonylation experiments had required thermal activation of 100 °C, it was observed that **2** reacted with one equivalent of PPh_3 cleanly at room temperature by substitution of one CO ligand. The ^{31}P NMR spectrum of the product shows one singlet at δ 5.2 ppm.

The ^{13}C NMR spectrum in the carbonyl region displays one sharp singlet at room temperature indicating rapid intermetallic CO exchange. As seen in Fig. 2 upon decreasing the temperature the signal broadens and coalescence is observed at $-53\,°C$. At $-86\,°C$ intermetallic CO exchange is not completely frozen out however it can be seen that there are two resonances at δ 210 ppm and δ 179 ppm in a 3/1 ratio as expected for phosphine substitution at Ir. The site of attack is presumably determined by the more pronounced tendency of Ir to produce 16 electron species via ring dissociation [9].

The IR spectrum of compound **3** is complicated due to the presence of both all terminal (**3a**), and carbonyl bridged (**3b**) isomers, as has been previously noticed in the related FeRh [2] and FeIr [4] complexes. The isomerization involves a change in the bonding mode of the (μ-C_7H_7) moiety between the two metals as shown.



3a



3b

Rapid equilibrium between these isomers would lead to interchange of carbonyl groups on Ru and hence explains the low temperature ^{13}C NMR spectrum. Clearly there is a very low activation energy for this process.

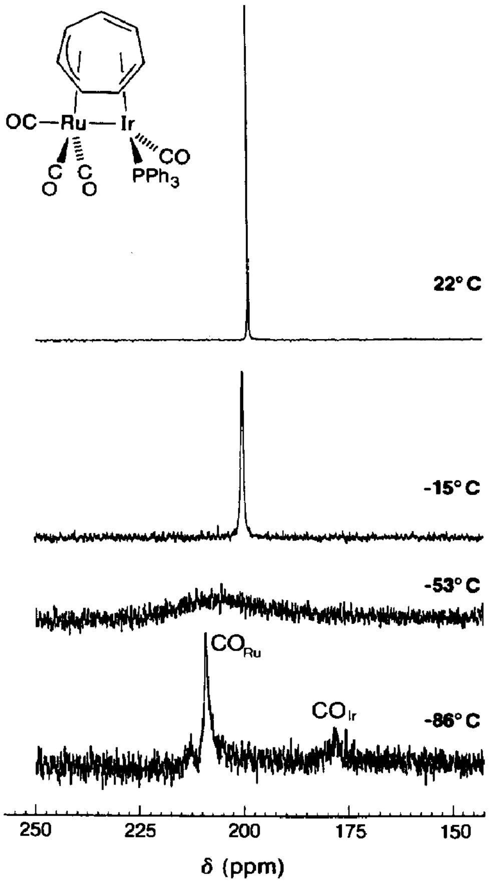
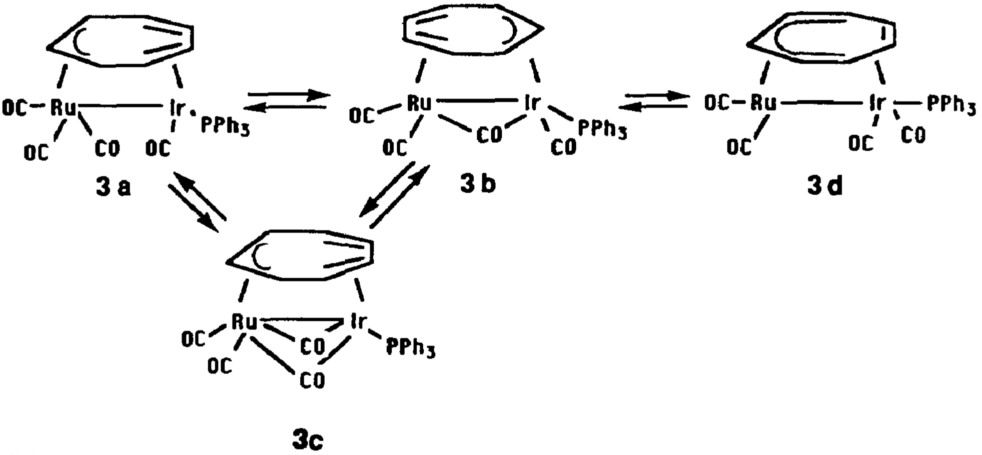


Fig. 2. Variable temperature ^{13}C NMR spectra of 3 in the carbonyl region.

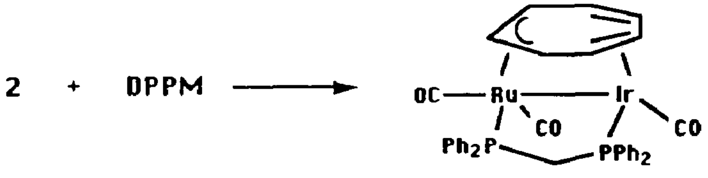
The free energy of activation for intermetallic carbonyl exchange calculated at the coalescence temperature [10] is 9.0 kcal/mol. This can be compared with the analagous complexes of RuRh (11.0 kcal/mol), FeIr (10.3 kcal/mol) and FeRh (15.4 kcal/mol). Of the several plausible intermediates available for this process, we have previously favoured the doubly bridged species **3c** (Scheme 1). The rationale behind our choice was that **3c** is easily achieved from both isomeric **3a** and **3b** while maintaining the μ-η^4,η^3-bonding functionality of the cycloheptatrienyl ring. However the surprising and unexpected trend of increasing facility for carbonyl group migration (Ru > Fe and Ir > Rh) is difficult to reconcile with this postulate since it is contrary to the well known greater reluctance of transition metals to accomodate bridging carbonyl groups upon descending a triad [11]. It now seems possible that an alternative intermediate (**3d**) which contains only terminal carbonyl ligands may also be involved in this process and may gain importance upon descending a triad. The necessary change in bonding mode of the cycloheptatrienyl ring to μ-η^5,η^2 may in this case dominate the energetics for global carbonyl scrambling, and account for the observed trend.

The reaction of **2** with bis(diphenylphosphino)methane (DPPM) was carried out under conditions similar to the reaction with PPh_3, but this time the displacement of two CO groups was observed. The IR spectrum of the product shows three bands,



Scheme 1

all in the terminal carbonyl stretching region at 1980, 1936, and 1914 cm^{-1}. Two doublets were observed in the ^{31}P NMR spectrum at δ 65.3 ppm (Ru) and δ 25.0 ppm (Ir) with typical P–P coupling constants of 125 Hz [12]. The ^{13}C NMR in the carbonyl region now shows three resonances at room temperature at δ 208 ppm (Ru), δ 196 ppm (Ru) and δ 183 ppm (Ir).



4

These data are characteristic [2,3] of the expected product (μ-C_7H_7)(μ-DPPM)$Ru(CO)_2Ir(CO)$ (**4**). The reaction was followed at room temperature by IR and ^{31}P NMR spectroscopy, which failed to give evidence for any intermediates. A reasonable explanation for this would be that the reaction proceeds via slow initial substitution at Ir, in a fashion similar to the PPh_3 reaction and this is followed by rapid substitution of a second carbonyl group at Ru leading to product formation. Unfortunately crystallisation failed to eliminate various phosphorus containing minor impurities which appeared erratically in the ^{31}P NMR spectrum. In addition, **4** appears less thermally stable and is considerably more air sensitive than **3**, which renders purification more difficult. The decrease in stability upon addition of phosphorus donor ligands is probably electronic in origin and perhaps opens new channels for competing reaction pathways leading to the unexpected minor byproducts. Due to these difficulties, complex **4** was not further investigated.

Conclusion

The synthesis of the series of complexes (μ-C_7H_7)$MM'(CO)_4L$ (M = Fe, Ru and M' = Rh, Ir: L = CO, PPh_3) has been completed. For L = PPh_3 a decrease in activation energy for intermetallic CO exchange is noticed on going from Fe to Ru and from Rh to Ir. Due to the necessary involvement of bridging carbonyl groups in this process, this is a surprising result in view of the greater tendency to accomodate bridging carbonyls for 1st row transition metals. It has however been noticed that substitution by phosphines increases the tendency for carbonyl groups to occupy bridging positions, and also the facility for carbonyl group migration [13]. This effect is dramatically demonstrated in the present case since whilst intermetallic CO scrambling is facile for the phosphine complex **3**, it is not observed in the pentacarbonyl complex **2**.

Experimental

All reactions were carried out under purified nitrogen using standard Schlenk techniques and carefully dried solvents. Bis(diphenylphosphino)methane (DPPM) was purchased from Pressure Chemical Company and triphenylphosphine and 1,5-cyclooctadiene (COD) from Aldrich, these materials were used as received. Ammonium hexachloroiridate(IV) was obtained from Engelhard. Potassium t-butoxide (KO^tBu) was purchased from Aldrich and sublimed prior to use (150 °C, 10^{-3} mmHg). $[Ir(COD)Cl]_2$ [14] and $(C_7H_8)Ru(CO)_3$ [5] were prepared according to literature methods.

Infrared spectra were obtained with a Nicolet MX-1 Fourier Transform Interferometer. Mass spectra were taken with an A.E.I. MS-12 spectrometer operating at 70eV or 16eV. NMR spectra were recorded on a Bruker WH 200, Bruker WH 400 or Bruker AM 300 spectrometer. Elemental analysis were performed by the Microanalytical Laboratory of this department.

(μ-C_7H_7)$Ru(CO)_3Ir(COD)$ (1)

$K(C_7H_7)Ru(CO)_3$ (4.60 mmol, 1.45 g) was prepared by the addition of equimolar quantities of KO^tBu in THF (20 ml) to $(C_7H_8)Ru(CO)_3$ in THF (40 ml) at −78 °C. The anion was transferred to a jacketed dropping funnel and cooled by dry-ice and was then added dropwise to a solution of $[Ir(COD)Cl]_2$ (2.30 mmol, 1.54 g) in THF (40 ml) at room temperature. The dark solution was stirred for 12 h at room temperature and evaporated to dryness. The brown residue was extracted with 2 aliquots of toluene (20 ml) and chromatographed on a 16 × 2.5 cm silica gel column (Merck, Kieselgel 60 mesh). Elution with hexane produced a large red band which was collected under nitrogen. The solvent was removed from the eluate and the residue was redissolved in hexane (20 ml) and cooled at −78 °C for 12 h to obtain yellow crystals (0.462 g, 17%). Concentration of the mother liquor to 2 ml yielded a final crop (0.140 g, 23% overall) m.p. 139 °C (dec).

Anal. Found: C, 37.66; H, 3.40. $C_{18}H_{19}IrO_3Ru$ calcd.: C, 37.49; H, 3.32%. Mass spectrum (70 eV, 90 °C); M^+, $M^+ - n$CO ($n = 1$–3). IR (hexane) ν(CO): 2038(s), 1977(s), 1970(s) cm^{-1}. ^1H NMR (25 °C, CD_2Cl_2): δ 3.82 (s, 7H, C_7H_7), 3.52 (m, 2H, CH_{COD}), 3.16 (m, 2H, CH_{COD}), 2.54 (m, 2H, $CH_{2\,COD}$), 2.24 (m, 2H, $CH_{2\,COD}$), 2.12 (m, 4H, $CH_{2\,COD}$). (−100 °C): δ 2.80 (br, 2H, C_7H_7), 3.54 (br, 1H, C_7H_7), 3.76 (br, 2H, C_7H_7), 4.72 (br, 2H, C_7H_7). ^{13}C {^1H} NMR (25 °C, CD_2Cl_2): δ 33.5 (s, $CH_{2\,COD}$), 34.7 (s, $CH_{2\,COD}$), 60.0 (s, C_7H_7), 63.4 (s, CH_{COD}), 64.4 (s, CH_{COD}), 196.8 (s, CO_{Ru}).

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (2)

(μ-C_7H_7)Ru(CO)$_3$Ir(COD) (90 mg, 0.16 mmol) was dissolved in octane (30 ml). The solution was degassed by two freeze-pump-thaw cycles. An atmosphere of CO was introduced to the reaction vessel, which was then heated at 100 °C for 2 h and then evaporated to dryness in vacuo. The residue was redissolved in hexane (5 ml), concentrated to 0.5 ml, and then cooled to −78 °C over 12 h to give yellow orange crystals of **2** (72 mg, 88%) m.p. 126–127 °C. Anal. Found: C, 27.94; H, 1.42. $C_{12}H_7IrO_5Ru$ calcd.: C, 27.48; H, 1.35%. Mass spectrum (70 eV, 110 °C): M^+, $M^+ - n$CO (n = 1-5). IR (hexane) ν(CO): 2066(s), 2019(s), 2005(s), 1984(m), 1973(w) cm^{-1}. ^{1}H NMR (25 °C, CD_2Cl_2): δ 4.16 (s, 7H, C_7H_7); (−100 °C): δ 3.24 (br, 2H, C_7H_7), 4.00 (br, 2H + 1H, C_7H_7), 5.24 (br, 2H, C_7H_7). ^{13}C {^{1}H} NMR (25 °C, CD_2Cl_2): δ 58.4 (s, C_7H_7), 175.4, (s, CO_{Ir}), 196.8 (s, CO_{Ru}).

Synthesis of ^{13}CO enriched sample

^{13}CO (99.1%) was purchased from Isotech Inc. Compound **2** was enriched in ^{13}CO by stirring an octane solution of **2** under 1 atm of ^{13}CO at 70 °C for 1 h. The enrichment was 94% as determined from the mass spectrum of the compound.

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)PPh$_3$ (3)

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (31 mg, 0.059 mmol) was dissolved in C_6H_6(15 ml), and the solution was degassed. PPh$_3$ (15.5 mg, 0.059 mmol) was added as a solid and the solution was stirred for 3 h, and then evaporated to dryness. The orange residue was washed once with hexane and then recrystallized from CH_2Cl_2/hexane at −78 °C to give orange red crystals of **3** (34 mg, 76%) m.p. 138–139 °C (dec). Anal. Found: C, 45.82; H, 2.98. $C_{29}H_{22}IrO_4PRu$ calcd.: C, 45.91; H, 2.92%. Mass Spectrum (70 eV, 180 °C): M^+, $M^+ - n$CO (n = 1–4). IR (C_6H_6) ν(CO): 2034(w), 2004(m), 1970(s,br), 1935(br), 1785(w,br) cm^{-1}. ^{1}H NMR (25 °C, C_6D_6): δ 7.6 (m, 2H, Ph, *o*), 7.1 (m, 2H, Ph, *m*), 7.0 (m, 1H, Ph, *p*), 3.56 (s, 7H, C_7H_7). ^{13}C {^{1}H} NMR (25 °C, CD_2Cl_2): δ 60.5 (s, C_7H_7), 128.6 (d, *J*(P–C) 10.5 Hz, Ph, *m*), 130.6 (s, Ph, *p*), 135.6 (d, *J*(P–C) 11.4 Hz, Ph, *o*), 136.0 (d, *J*(P–C) 40 Hz, Ph, *ipso*), 199.7 (s, CO, averaged); (−86 °C): δ 209.6 (s, CO_{Ru}), 179.3 (s, CO_{Ir}). ^{31}P {^{1}H} NMR (25 °C, C_6D_6): δ 5.15 (s, PPh$_3$).

(μ-C_7H_7)Ru(CO)$_2$Ir(CO)(μ-DPPM) (4)

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (25 mg, 0.048 mmol) was dissolved in toluene (15 ml) and the solution was degassed. DPPM (18.3 mg, 0.048 mmol) was added as a solid. The solution was stirred for 3 h during which time starting material was consumed and **4** was formed as monitored by IR spectroscopy. The solution was then concentrated to 0.5 ml and layered with hexane (2 ml). The vessel was then cooled at −78 °C to give a bright orange, air sensitive solid, **4** which was analysed immediately by NMR spectroscopy, m.p. 75 °C (dec). Anal. Found: C, 47.88; H, 3.86. $C_{35}H_{29}IrO_3P_2Ru$ calcd.: C, 49.29; H, 3.43%. Mass Spectrum (70 eV, 200 °C): M^+, $M^+ - n$CO, (n = 1–3). IR (benzene) ν(CO): 1980(s), 1936(s), 1914(m) cm^{-1}. ^{1}H NMR (25 °C, C_6D_6): δ 7.7–6.8 (m, 20H, Ph), 3.82 (dt, 1H, *J*(H–H) 14 Hz, *J*(H–P) 12 Hz, CH_2), 3.65 (s, 7H, C_7H_7), 2.11 (dt, 1H, *J*(H–H) 14 Hz, *J*(H–P) 8 Hz, CH_2). ^{13}C {^{1}H} NMR (25 °C, toluene-d_8): δ 208.2 (s, CO_{Ru}), 195.7 (d, *J*(P–C) 9 Hz, CO_{Ru}), 182.7 (d, *J*(P–C) 9 Hz, CO_{Ir}), 138.2–129.3 (Ph), 57.2 (s, C_7H_7), 42.2 (dd, *J*(P–C) 24, 41 Hz, CH_2). ^{31}P {^{1}H} NMR (25 °C, C_6D_6): δ 65.3 (d, *J*(P–P) 125 Hz, Ru–P), 25.0 (d, *J*(P–P) 125 Hz, Ir–P).

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