Conversion of Uncharged Methyl Complexes of Ruthenium(II) into a Cationic Acyl Complex: a Mechanistic Study

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Spectroscopic studies of the reactions of methyl complexes $[Ru(CO)_2(Me)X(PMe_2Ph)_2]$ [X = Cl, (**1a**); X = I, (**1b**)] with Me_3CNC have revealed that the end-product, $[Ru(CO)(CNCMe_3)_2(COMe)(PMe_2Ph)_2]^+$ (**2**), is formed *via* two isomers of the complexes $[Ru(CO)(CNCMe_3)(COMe)X(PMe_2Ph)_2]$ [X = Cl, (**3a**) and (**4a**); X = I, (**3b**) and (**4b**)]. Formation of the kinetically favoured isomers (**3a**) and (**3b**), from (**1a**) and (**1b**) respectively, is very rapid, while the relative rates of the isomerization and the further reaction with Me_3CNC to yield (**2**) vary with the solvent and the halide ion X^-. Two alternative mechanisms for the isomerization, involving dissociation of the isonitrile or the halide ligand, are discussed.

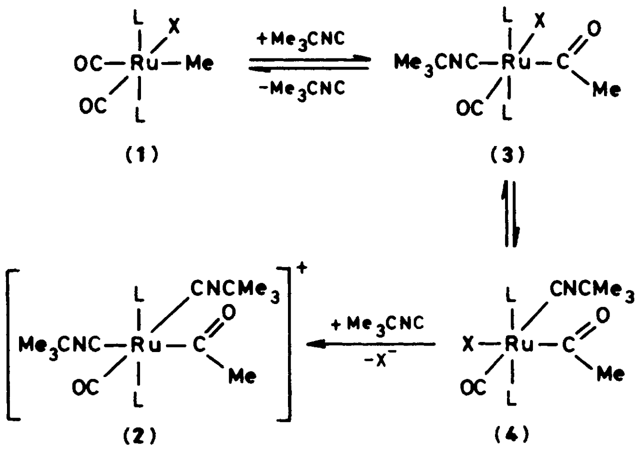
We have recently described the unusual case of the reactions of phenyl complexes of ruthenium(II), $[Ru(CO)_2(C_6H_4Y\text{-}4)X(PMe_2Ph)_2]$, with Me_3CNC, where the balance between two quite different modes of reaction is so delicately poised that it can be greatly affected by varying the *para* substituent Y in the phenyl ring. Changes in the anionic ligand X^- have an even more marked effect. The two types of reaction are a straightforward substitution of a carbonyl ligand, yielding $[Ru(CO)(CNCMe_3)(C_6H_4Y\text{-}4)X(PMe_2Ph)_2]$, and the formation of benzoyl complexes $[Ru(CO)(CNCMe_3)_2(COC_6H_4Y\text{-}4)(PMe_2Ph)_2]^+$. Although the latter reaction presumably involves more than one step, spectroscopic studies failed to reveal the presence of any intermediates, making it impossible to be certain whether the combination of phenyl and carbonyl ligands occurred in the first step, or whether it was preceded by substitution of the ligand X^- to yield $[Ru(CO)_2(CNCMe_3)(C_6H_4Y\text{-}4)(PMe_2Ph)_2]^+$.[1]

Earlier work had shown that the related methyl complexes $[Ru(CO)_2(Me)X(PMe_2Ph)_2]$ (X = Cl, Br, or I) react extremely rapidly with CO or PMe_2Ph to give acetyl complexes $[Ru(CO)(COMe)X(PMe_2Ph)_2L']$ (L′ = CO or PMe_2Ph).[2] We were interested to determine whether the methyl complexes, like their phenyl counterparts, would react with Me_3CNC to give a cationic acyl complex, $[Ru(CO)(CNCMe_3)_2(COMe)(PMe_2Ph)_2]^+$. If so, assuming that the first step in the reactions involved the formation of intermediates $[Ru(CO)(CNCMe_3)(COMe)X(PMe_2Ph)_2]$, and that the rate of the subsequent substitution of the halide ligand X^- would be much the same for $[Ru(CO)(CNCMe_3)(COMe)X(PMe_2Ph)_2]$ as for $[Ru(CO)(CNCMe_3)(COC_6H_4Y\text{-}4)X(PMe_2Ph)_2]$, we clearly stood a much better chance of observing such intermediates in these reactions than in the reactions of the phenyl complexes.

Results and Discussion

Formation of New Complexes.—Details of the i.r., ^1H n.m.r., and ^{13}C n.m.r. spectra of new complexes discussed in this section are given in Tables 1, 2, and 3 respectively. Structures of the complexes are shown in Scheme 1.

The reaction of $[Ru(CO)_2(Me)Cl(PMe_2Ph)_2]$ (**1a**) [structure (**1**); L = PMe_2Ph, X = Cl] with Me_3CNC in a 1:2 molar ratio was carried out at ambient temperature in $CDCl_3$ solution. After 5 h, the ^1H n.m.r. spectrum of the solution indicated the presence of a single ruthenium complex. Singlet resonances were observed whose chemical shifts and relative areas were as expected for an acetyl ligand and two inequivalent Me_3CNC ligands. The spectrum also contained the triplet resonance expected for the methyl protons in a pair of mutually *trans* PMe_2Ph ligands.† An i.r. study of the same reaction in $CHCl_3$ solution confirmed that the product contained two (mutually *cis*) Me_3CNC ligands and an acyl ligand, and also indicated the presence of a carbonyl ligand. We concluded that the reaction had yielded $[Ru(CO)(CNCMe_3)_2(COMe)(PMe_2Ph)_2]^+$ [structure (**2**); L = PMe_2Ph]. Evidently the difference in chemical shift between the two inequivalent sets of PMe_2Ph methyl protons (the inequivalence being due to the fact that the Ru–P bonds do not lie in a molecular symmetry plane) was too small to detect. The corresponding inequivalence between the methyl carbon atoms was, however, detected in the ^{13}C n.m.r. spectrum, which also contained the other resonances expected for cation (**2**). When the reaction was repeated in PhCl solution, the ^1H n.m.r. spectrum of the product was (apart from minor changes in chemical shifts) the same as that in $CDCl_3$ solution, except that there were now two triplet resonances of equal area (at δ 1.87 and 1.82) for the PMe_2Ph methyl protons.



Scheme 1.

We were unable to obtain the chloride salt of the cation (**2**) in the solid state, but treatment of a propanone solution of the salt with an equimolar quantity of $NaBPh_4$ yielded $[Ru(CO)(CNCMe_3)_2(COMe)(PMe_2Ph)_2]BPh_4$, which was

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† The ways in which phosphorus ligands may be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[3,4]

isolated as a solid and fully characterized. The reaction of [Ru(CO)$_2$(Me)I(PMe$_2$Ph)$_2$] (**1b**) with Me$_3$CNC in a 1:2 molar ratio was studied by ^{1}H n.m.r. spectroscopy in both CDCl$_3$ and PhCl solution, and again the end-product was identified as the cation (**2**).

Having established that both (**1a**) and (**1b**) reacted with Me$_3$CNC to give an acetyl complex analogous to the benzoyl complexes [Ru(CO)(CNCMe$_3$)$_2$(COC$_6$H$_4$Y-4)(PMe$_2$Ph)$_2$]$^+$ formed by phenyl complexes [Ru(CO)$_2$(C$_6$H$_4$Y-4)X-(PMe$_2$Ph)$_2$], we looked for evidence of intermediates formed during the conversion of (**1a**) and (**1b**) into (**2**). Treatment of a CDCl$_3$ solution of (**1a**) with an equimolar quantity of Me$_3$CNC resulted in immediate and complete formation of a product (**3a**), whose ^{1}H n.m.r. spectrum included resonances attributable to a pair of mutually *trans* PMe$_2$Ph ligands, an acetyl ligand, and one Me$_3$CNC ligand. An i.r. study of the reaction in CHCl$_3$ solution confirmed that (**3a**) contained acetyl and isonitrile ligands, and indicated the presence of a carbonyl ligand. On the basis of the spectroscopic evidence, (**3a**) was assigned the formula [Ru(CO)(CNCMe$_3$)(COMe)Cl(PMe$_2$Ph)$_2$]. From the n.m.r. and i.r. studies, however, it was evident that (**3a**) subsequently reached equilibrium with another species, (**4a**), with a final (**3a**):(**4a**) ratio of approximately 30:70. The spectra of (**4a**) contained bands similar to those of (**3a**) but somewhat altered in position, suggesting that (**4a**) was another isomer of [Ru(CO)(CNCMe$_3$)(COMe)Cl(PMe$_2$Ph)$_2$], again containing a mutually *trans* pair of PMe$_2$Ph ligands. We had previously obtained similar pairs of isomers of complexes [Ru(CO)(COMe)X(PMe$_2$Ph)$_2$L′] (X = Br or I, L′ = CO or PMe$_2$Ph) as products of the reactions of [Ru(CO)$_2$(Me)X-(PMe$_2$Ph)$_2$] with CO and PMe$_2$Ph, and had shown unambiguously in the case of L′ = PMe$_2$Ph that L′ was *trans* to the newly formed acetyl ligand in the first-formed isomer and *trans* to the carbonyl ligand in the other isomer.[2] Hence we concluded that the structures of (**3a**) and (**4a**) were those shown in Scheme 1 [(3) and (4); L = PMe$_2$Ph, X = Cl]. {Confusingly, Pankowski and Bigorgne,[5] who observed a similar isomerization of [Ru(CO)$_2$(COMe)I(PMe$_3$)$_2$], formed by treatment of [Ru(CO)$_2$(Me)I(PMe$_3$)$_2$] with CO, claimed to have proved that the first-formed isomer of [Ru(CO)$_2$(COMe)I(PMe$_3$)$_2$] resulted from attack by CO *cis* to the acetyl ligand. In fact, as Wright and Baird[6] have pointed out, the results obtained by Pankowski and Bigorgne[5] cannot distinguish between attack *cis* or *trans* to the acetyl ligand.}

Table 1. Infrared spectra of complexes[a]

Complex	ν(C–N)/cm^{-1}	ν(C–O)/cm^{-1}
(**2**)[b]	2 200, 2 170	2 010, 1 595
(**2**)[c]	2 200, 2 170	2 010, 1 595
(**3a**)	2 170	1 960, 1 575
(**4a**)	2 180	1 990, 1 580
(**4b**)	2 180	1 985, 1 590

[a] In CHCl$_3$ solution; only bands due to nitrile and carbonyl stretching modes are listed. [b] Chloride salt. [c] Tetraphenylborate salt.

Table 2. Proton n.m.r. spectra (δ values) of complexes[a]

Complex	CNCMe$_3$	COMe	PMe$_2$Ph[b]
(**2**)[c]	1.53 (s, 9) 1.31 (s, 9)	2.05 (s, 3)	1.89 (t, 12)[d]
(**2**)[e]	1.32 (s, 9) 1.10 (s, 9)	2.05 (s, 3)	1.72 (t, 6) 1.70 (t, 6)
(**2**)[f]	1.55 (s, 9) 1.34 (s, 9)	2.04 (s, 3)	1.92 (t, 12)[d]
(**3a**)	1.00 (s, 9)	2.23 (s, 3)	1.84 (t, 6) 1.79 (t, 6)
(**4a**)	1.24 (s, 9)	1.71 (s, 3)	1.86 (t, 6) 1.81 (t, 6)
(**3b**)[g]	0.84 (s, 9)	2.70 (s, 3)	1.94 (t, 6) 1.81 (t, 6)
(**4b**)	1.31 (s, 9)	1.73 (s, 3)	2.02 (t, 12)[d,h]

[a] In CDCl$_3$ solution, unless stated otherwise; resonances due to phenyl protons are not included. [b] $|^2J(\text{P–H}) + {}^4J(\text{P–H})|$ = *ca.* 7 Hz. [c] Chloride salt. [d] Inequivalence of resonances too small to detect. [e] Tetraphenylborate salt. [f] Iodide salt. [g] In PhCl solution. [h] Resonance resolved into two triplets (δ 2.00 and 1.96) of equal area at 273 K.

Both the rate of isomerization of (**3a**) and the position of equilibrium were affected by the choice of solvent: in PhCl, for example, equilibrium was reached in days (as opposed to hours in CHCl$_3$), and the balance between (**3a**) and (**4a**) was approximately 50:50. By carrying out the reaction between equimolar quantities of (**1a**) and Me$_3$CNC in benzene solution at 280 K, we were actually able to isolate and characterize a pure sample of (**3a**). A ^{13}C n.m.r. spectrum of (**3a**) in CDCl$_3$ solution was obtained at 253 K (at which temperature isomerization was very slow), and from a spectrum of the equilibrium mixture of (**3a**) and (**4a**), also recorded at 253 K, we could then identify the resonances due to (**4a**).

The reaction between equimolar quantities of the iodo-complex (**1b**) and Me$_3$CNC in CDCl$_3$ or PhCl solution yielded isomers (**3b**) and (**4b**) of [Ru(CO)(CNCMe$_3$)(COMe)I-(PMe$_2$Ph)$_2$]. Again one isomer, (**3b**), was formed immediately and quantitatively, but the subsequent conversion into (**4b**) was also essentially quantitative. The fact that the thermodynamic preference for structure (4) over (3) is greater in the case of [Ru(CO)(CNCMe$_3$)(COMe)I(PMe$_2$Ph)$_2$] than it is for [Ru(CO)(CNCMe$_3$)(COMe)Cl(PMe$_2$Ph)$_2$] presumably reflects the bulkier nature of the iodide ligand and the consequent

Table 3. Carbon-13 n.m.r. spectra (δ values) of complexes[a]

Complex	CO[b]	*C*OMe[c]	CO*Me*	CN*C*Me$_3$	CNC*Me*$_3$	P*Me*$_2$Ph[d]
(**2**)[e]	196.5	259.5	49.5	58.5 57.9	29.5 29.3	16.7 16.2
(**2**)[f]	197.7	259.6	50.2	59.0 58.4	29.9 29.8	17.1 16.6
(**3a**)	199.0	273.4	44.5	56.2	29.6	14.1 13.9
(**4a**)	200.1	256.7	48.6	56.8	29.8	15.5 15.2
(**4b**)	200.1	255.4	47.9	57.0	29.9	18.5 18.0

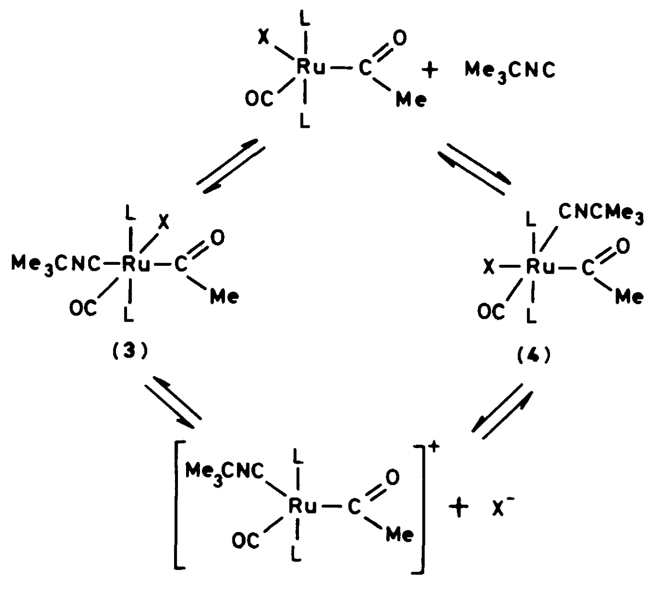
[a] In CDCl$_3$ solution; resonances for phenyl carbon atoms and the weak broad resonances for *C*NCMe$_3$ have been omitted. Unless indicated otherwise, resonances are singlets. [b] Triplet resonances: $|^2J(\text{P–C})|$ = *ca.* 13 Hz. [c] Triplet resonances: $|^2J(\text{P–C})|$ = *ca.* 11 Hz [8 Hz for complex (**4b**)]. [d] Triplet resonances: $|^1J(\text{P–C}) + {}^3J(\text{P–C})|$ = *ca.* 33 Hz. [e] Chloride salt. [f] Tetraphenylborate salt.

repulsion between mutually *cis* iodide and acetyl ligands in (**3b**). Conversion into (**4b**) was also considerably faster than in the case of the chloro-complex. In $CDCl_3$ solution, (**3b**) could only be detected when the reaction was carried out at 273 K rather than ambient temperature. As in the case of the chloro-complex, isomerization was slower in PhCl solution, but even in this solvent the conversion of (**3b**) into (**4b**) was complete at ambient temperature within 0.5 h. Complex (**4b**) was isolated from a reaction between (**1b**) and Me_3CNC in $CHCl_3$ solution and fully characterized.

Mechanism of Conversion of (**1a**) *and* (**1b**) *into* (**2**).—When the reaction between (**1a**) and Me_3CNC in a 1:2 molar ratio in $CDCl_3$ solution at ambient temperature was monitored by ^1H n.m.r. spectroscopy, immediate conversion of (**1a**) into (**3a**) was followed by the appearance of resonances due to (**4a**) and (**2**). The concentration of (**4a**) soon reached a maximum; thereafter the resonances due to both (**3a**) and (**4a**) weakened and finally disappeared as conversion to (**2**) was completed. In a study of the same reaction in PhCl solution, (**4a**) was not observed: as the resonances due to (**3a**) weakened, only those due to (**2**) appeared. Complete conversion into (**2**) was also much slower than in $CDCl_3$ solution. The failure to observe (**4a**) prompted us to treat an equilibrium mixture of (**3a**) and (**4a**) [as obtained from the reaction of equimolar quantities of (**1a**) and Me_3CNC in PhCl solution] with more Me_3CNC. Within a few hours, (**4a**) was completely converted into (**2**), whereas there was little change in the concentration of (**3a**). It then took several days for the conversion of (**3a**) into (**2**) to reach completion.

From these results we concluded that there was a direct route from (**4a**) to (**2**). A simple explanation of our observations (Scheme 1; L = PMe_2Ph, X = Cl) would be that (**1a**) reacted rapidly to form (**3a**), (**3a**) isomerized to (**4a**), and (**4a**) was converted into the final product, (**2**), the substitution of the chloride ligand being assisted by the strong *trans*-labilizing effect of the acetyl ligand.[2,7] In $CDCl_3$ solution the steps (**3a**) ⟶ (**4a**) and (**4a**) ⟶ (**2**) were comparable in rate, whereas in PhCl the former was considerably slower than the latter. We could not, however, rule out the possibility that there was a separate direct route from (**3a**) to (**2**). Studies of the reaction of (**1b**) with Me_3CNC were not particularly helpful because of the more rapid (and complete) isomerization of (**3b**) to (**4b**). In $CDCl_3$ solution, at ambient temperature, the only species observed were (**4b**) and (**2**). In PhCl, (**3b**) was observed early in the reaction, but conversion into (**4b**) was complete at a stage when only a small amount of (**2**) had been formed. Again the sequence of steps shown in Scheme 1 (L = PMe_2Ph, X = I) was compatible with the results, but with the isomerization step now rapid compared with the subsequent formation of (**2**).

The mechanism of the isomerization (**3**) ⟶ (**4**) was also considered. In the reactions of the complexes $[Ru(CO)_2(Me)X(PMe_2Ph)_2]$ (X = Cl, Br, or I) with CO or PMe_2Ph, there is n.m.r. evidence of the lability of the bond to the ligand L′ in the first-formed isomer of the products $[Ru(CO)(COMe)X(PMe_2Ph)_2L']$ (L′ = CO or PMe_2Ph), and on this basis we suggested that the isomerization involved dissociation of this ligand and subsequent attack on the intermediate $[Ru(CO)(COMe)X(PMe_2Ph)_2]$ *trans* to CO.[2] To determine whether the bond to the isonitrile ligand in (**3a**) exhibited similar lability, we treated (**1a**) in PhCl solution with half the quantity of Me_3CNC required for complete conversion into (**3a**). The temperature of the solution, now containing equal quantities of (**1a**) and (**3a**), was raised in steps of 10 °C. This caused (**3a**) to come into equilibrium with (**4a**), but it also caused the acetyl proton resonance of (**3a**) and the resonance for the protons in the methyl ligand of (**1a**) to broaden, until at 333 K they had almost completely collapsed. When the solution was cooled to ambient temperature, the resonances sharpened again [the acetyl resonance for (**4a**) did not alter in appearance over the temperature range studied]. Hence there was evidence for a rapid equilibrium between (**1a**) and (**3a**), and thus for rapid and reversible loss of the isonitrile ligand from (**3a**).



Scheme 2.

This, then, provided support for isomerization by dissociation of the isonitrile ligand, as shown in the upper part of Scheme 2 (L = PMe_2Ph, X = Cl), *via* the intermediate $[Ru(CO)(COMe)Cl(PMe_2Ph)_2]$ which we have previously assumed[2] to be five-co-ordinate, but which might alternatively contain an η^2-bonded acyl ligand, as has been shown to be the case for the related complexes $[Ru(CO)(COMe)I(PPh_3)_2]$ and $[Ru(CO)(COC_6H_4Me\text{-}4)I(PPh_3)_2]$ in the solid state.[8]

Of course the observation that the bond to the isonitrile ligand in (**3a**) is labile does not *prove* that isomerization occurs, either wholly or in part, by dissociation of this ligand, and there remains the possibility that isomerization can occur by loss of the halide ligand, as shown in the lower part of Scheme 2. Pankowski and Bigorgne[5] have suggested a similar mechanism for the isomerization of $[Ru(CO)_2(COMe)I(PMe_3)_2]$. Such a mechanism would automatically also provide a direct route from (**3a**) to (**2**) (see above). We found that the rate of isomerization of (**3a**) to (**4a**) increased with the nature of the solvent in the order C_6D_6 < PhCl < CD_3COCD_3 < $CDCl_3$, and that it was further increased by the addition of a little water to either the CD_3COCD_3 or the $CDCl_3$. These results are compatible with a mechanism involving dissociation into charged species, except that $CDCl_3$ is out of place in the sequence (having a lower dielectric constant than either PhCl or propanone[9]). Isomerization in CD_3COCD_3 and in $CDCl_3$ was not inhibited by free chloride ion, but this does not rule out dissociation of Cl^- provided that the mechanism involves a single intermediate rather than two separate square-pyramidal forms of $[Ru(CO)(CNCMe_3)(COMe)(PMe_2Ph)_2]^+$.

Experimental

Complexes were prepared and reactions studied under an atmosphere of dry nitrogen. Details of the instruments used to obtain i.r. and ^1H and ^{13}C n.m.r. spectra have been given elsewhere,[10] as have the preparations of complexes (**1a**) and (**1b**).[2,11] Studies of the isomerization of (**3a**) were performed by ^1H n.m.r. spectroscopy and also by ^{31}P n.m.r. spectroscopy, using a JEOL FX-90Q spectrometer with an operating frequency for ^{31}P of 36.2 MHz.

Isolation of the Tetraphenylborate Salt of Cation (**2**).—To a solution of complex (**1a**) (0.15 g) in $CHCl_3$ (5 cm^3) was added Me_3CNC (0.071 cm^3). After 24 h, the solvent was removed by evaporation under a stream of nitrogen. The oily residue, together with $NaBPh_4$ (0.10 g), was dissolved in propanone (10 cm^3). Slow evaporation of the solvent under a stream of nitrogen left a colourless oil which was crystallized from a 1:1 mixture of propanone and ethanol. The colourless crystals were washed with ethanol (yield 85%) (Found: C, 67.7; H, 6.70; N, 3.20. Calc. for $C_{53}H_{63}BN_2O_2P_2Ru$: C, 68.15; H, 6.80; N, 3.00%).

Isolation of Complex (**3a**).—A stirred solution of complex (**1a**) (0.13 g) in benzene (2 cm^3) was treated with Me_3CNC (0.030 cm^3) at 280 K. After 1 min, the solvent was removed, still at 280 K, under reduced pressure, and the colourless solid obtained was dried *in vacuo* for a further 2 h (yield 100%) (Found: C, 51.6; H, 5.95; N, 2.45. Calc. for $C_{24}H_{34}ClNO_2P_2Ru$: C, 50.85; H, 6.05; N, 2.45%).

Isolation of Complex (**4b**).—A solution of complex (**1b**) (0.20 g) and Me_3CNC (0.040 cm^3) in $CHCl_3$ (10 cm^3) was stirred in the absence of light for 10 min. Slow evaporation of the solvent under a stream of nitrogen gave colourless crystals, which were recrystallized from a mixture of $CHCl_3$ (45%), ethanol (45%), and light petroleum (10%) (b.p. 313—333 K) (yield 93%) (Found: C, 43.95; H, 5.30; N, 2.30. Calc. for $C_{24}H_{34}INO_2P_2Ru$: C, 43.8; H, 5.20; N, 2.15%).

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