Modelling the Reduction of Nitrobenzene with $[Ru_3(CO)_{12}]$ as a Homogeneous Catalyst. *X*-Ray Structures of $[Ru_3H(CO)_{10}(PhNH)]$ and $[N(PPh_3)_2][Ru_3H(CO)_9(PhN)]$†

Sumit Bhaduri,* Hanif Khwaja, Niteen Sapre, Krishna Sharma, and Amitabha Basu
Alchemie Research Centre, P.O. Box 155, Thane 400 601, Maharashtra, India
Peter G. Jones
Institut Fur Anorganische und Analytische Chemie Der Technischen Universitat, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany
Gene Carpenter
Department of Chemistry, Brown University, Providence, RI 02912, U.S.A.

The ability of $[Ru_3(CO)_{12}]$ to act as a homogeneous catalyst in the reductive carbonylation of nitrobenzene has been confirmed. Under the conditions used in the catalytic runs the reactivities of the six clusters $[Ru_3(CO)_{10}(\mu_3\text{-PhN})]$ (**1**), $[Ru_3H(CO)_{10}(PhNH)]$ (**2**), $[Ru_3H_2(CO)_9(\mu_3\text{-PhN})]$ (**3**), $[Ru_3H(CO)_9(\mu_3\text{-PhNCO})]^-$ (**4**), $[Ru_3H(CO)_9(\mu_3\text{-PhN})]^-$ (**5**), and $[Ru_3(CO)_{10}(\mu\text{-PhNCHO})]^-$ (**6**) are described. The syntheses of (**4**)—(**6**) and the *X*-ray structures of (**2**) and (**5a**), the $[N(PPh_3)_2]^+$ salt of (**5**), are also discussed. The conversion of complex (**4**) into (**5**) has been studied kinetically. The activation parameters and a Hammett correlation for this reaction are reported. From the observed reactivities of (**1**)—(**6**), two model catalytic cycles for catalytic systems with or without OR^- (R = H or Me) as promoters have been proposed. Clusters (**4**) and (**6**) are probable catalytic intermediates in RO^--promoted catalytic runs.

Novel catalytic systems for nitrobenzene reduction and carbonylation are of considerable importance.[1] A number of reports have appeared on the reductive carbonylation of $PhNO_2$ with $[Ru_3(CO)_{12}]$ as a homogeneous catalyst. Various systems differing in detail have been described[2–5] for the syntheses of $PhNH_2$, PhNHCHO, $PhNHCO_2Me$, and PhNCO with high selectivities. It has been shown that addition of anions such as halides, hydroxides, or alkoxides has remarkable effects on the activities and selectivities of the catalytic systems.[3,4] Thus, while halides in alcoholic solvents favour the formation of carbamate esters,[4] hydroxide[3b–3d] and methoxide ions[3a] are known to promote the formation of $PhNH_2$ and PhNHCHO respectively. Finally the use of a co-ordinating solvent such as acetonitrile has been found[5] to give moderate to good yields of PhNCO.

Relatively little is known about the nature and identities of the intermediates that are involved in these reaction systems. Studies of the reactivity of metal clusters containing μ_3-NPh ligands and of their relevance in some of these catalytic systems have recently been reported.[6–8] Thus it has been shown that the μ_3-NPh ligand can couple with co-ordinated benzoyl and methoxy carbonyl groups in an intramolecular fashion to give, after oxidative degradation, benzanilide and $PhNHCO_2Me$ respectively.[6] It has also been established that, under forcing conditions, the μ_3-NPh ligand can couple with CO.[7] However, on addition of halide ions the coupling reaction takes place under mild conditions.[9]

The work reported here was undertaken to investigate two main aspects. First, an exploration of the reactions of neutral clusters containing μ_3-NPh and μ-NHPh ligands, with a view to understanding their role, if any, in the catalytic systems. Secondly, an investigation into the mode of action of RO^- (R = H or Me) as promoters in the catalytic systems. This is of obvious importance since, with OH^- as a promoter, excellent conversion of nitrobenzene into aniline can be achieved at temperatures $\leqslant 68$ °C and atmospheric pressure of CO.[3b–d] Also, the use of OMe^- instead of OH^- under the same conditions is known to give PhNHCHO in good yields.[3a]

In this work (after structural characterisations wherever necessary) we have subjected ruthenium clusters containing μ-NHPh, μ_3-NPh, 'PhNCO', and 'PhNCHO' to reaction conditions used for the reductive carbonylation of nitrobenzene. For each reaction, nearly all the products have been identified. On the basis of these reactions, two hypothetical catalytic cycles have been proposed as models. Parts of this work have been reported earlier.[10,11]

Results and Discussion

(*a*) *Catalytic Reduction of Nitrobenzene.*—The ability of $[Ru_3(CO)_{12}]$ to act as a catalyst for the reductive carbonylation of nitrobenzene (leading to different products under different conditions) has been reconfirmed. These studies have been limited to systems without OH^- or OMe^- as promoters. It has been found that PhNCO is formed selectively in the complete absence of protic impurities. In the presence of trace quantities of moisture a mixture of PhNCO, $(PhNH)_2CO$, and $PhNH_2$ is obtained (see Experimental section). It should be noted that PhNCO and $PhNH_2$ react almost instantaneously to give $(PhNH)_2CO$. Aniline could be made selectively with high conversions by using a mixture of CO and H_2 or by carrying out the reaction in an alcoholic solvent. In the latter case the alcohol is oxidised to the corresponding carbonyl compound. Use of literature techniques indicates that cluster decomposition

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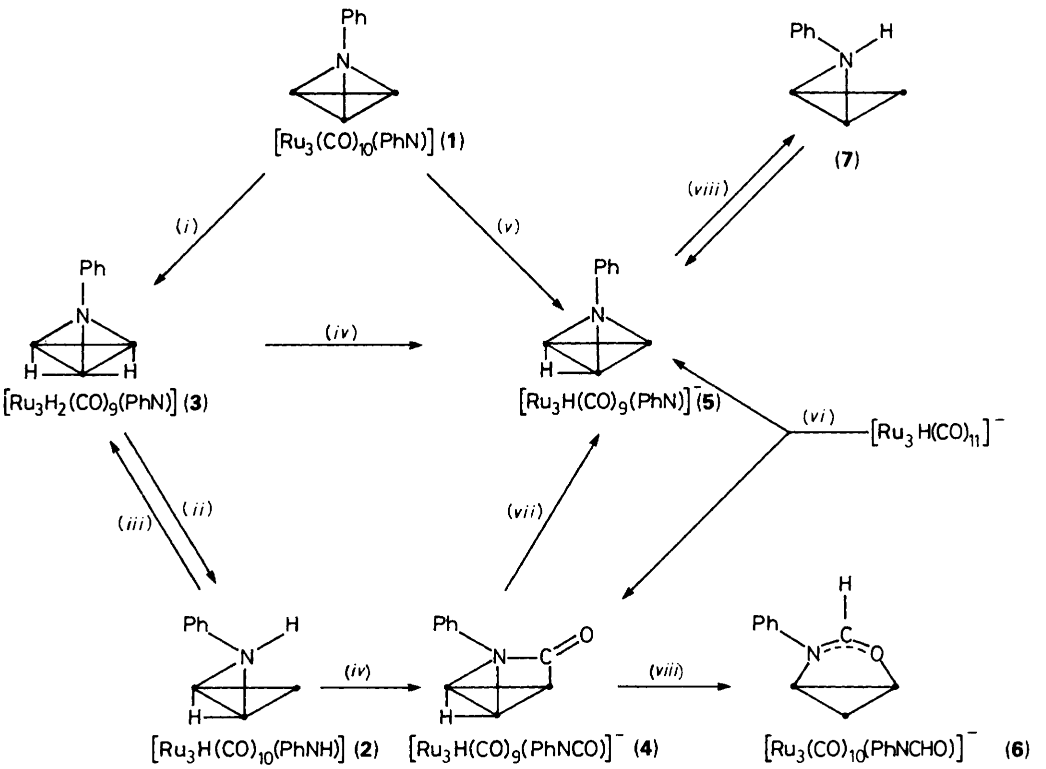
† 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-phenylamido-*triangulo*-triruthenium and bis(triphenylphosphine)iminium 1,3-μ-hydrido-μ₃-phenylimido-tris(tricarbonylruthenate) (Ru¹–Ru²).

Supplementary data available: Further details of the structure determination (complete bond angles, H-atom co-ordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54077.

Non-S.I. units employed: cal = 4.184 J, lbf in^{-2} = 6 895 Pa.



Scheme 1. (*i*) H_2, 60 °C; (*ii*) CO, 80 °C; (*iii*) 98 °C; (*iv*) OH^-; (*v*) BH_4^-; (*vi*) $PhNO_2$ or PhNO; (*vii*) $\geqslant 30$ °C; (*viii*) CO; • = Ru, carbonyl groups not shown

to metal does not take place during any of these catalytic runs.*

(*b*) *Synthesis of Clusters with Amido,* μ_3-NPh, 'PhNCO', *and* 'PhNCHO' *Ligands.*—The pictorial representations, designations, and selected reactions of some of the clusters discussed here are shown in Scheme 1. The structures of (**1**),[12] (**3**),[13] (**4**),[10] and (**6**)[11] have been reported. In this work the structures of complexes (**2**) and (**5**) have been established by single-crystal *X*-ray diffraction (see below). Syntheses of (**1**)—(**3**) were first reported by Sappa and Milone.[14] A better synthesis of (**1**), involving the reaction of $[Ru_3(CO)_{12}]$ with PhNO rather than $PhNO_2$, has been reported by us and others.[15,†]

All attempts to generate an isolable PhNCO-containing cluster by the carbonylation of (**1**) under a variety of thermal and photochemical conditions failed. The reactions of alkyl and aryl isocyanates with the unsaturated cluster $[Os_3H_2(CO)_{10}]$ and its derivatives have been reported.[16c—e] However neither in this case nor in the reaction of $[Ru_3(CO)_{12}]$ with PhNCO could a cluster containing bonded isocyanate be isolated. We therefore resorted to an alternative strategy for the synthesis of cluster-bound PhNCO. We reasoned that treatment of complex (**2**) with OH^- would result in the abstraction of the proton from the bridging amido group rather than the metal framework. This would generate a μ-NPh^- moiety, a nucleophile capable of attacking the CO group nearest to it and generating a cluster-bound PhNCO ligand. A similar argument has been used[17] to rationalise the formation of $[Os_3H_2(CO)_8(PMe_2Ph)(Bu^tCH{=}NNCO)]$ from the reaction of $[Os_3H_2(CO)_9(PMe_2Ph)]$ and Bu^tCHN_2. Indeed the reaction of (**2**) with equimolar base in methanol leads to the formation of (**4**) in good yields.

Cluster (**5**) may be synthesised in three different ways. First, under ambient conditions (**4**) loses CO slowly in solution to give (**5**) quantitatively. At slightly higher temperature ($\leqslant 55$ °C) this reaction is complete in a few minutes. Secondly, reaction of (**1**) with $NaBH_4$ gives (**5**) in good ($\leqslant 80\%$) yields. It should be noted that halide attack on (**1**) leading to the formation of $[Ru_3(CO)_9(\mu_3\text{-}PhN)X]^-$ (X = Cl, Br, or I) has been recently reported.[9] However, unlike the halide reaction, the reaction between (**1**) and $NaBH_4$ does not result in the formation of PhNCO when carried out under CO; complex (**5**) is stable under CO. The third synthesis of (**5**) is by the reaction of (**3**) with OH^-.

Cluster (**6**) can be made quantitatively by carbonylating (**4**) at ambient temperature under slightly elevated pressure (80 lbf in^{-2}) of CO. The carbonylation occurs slowly ($t_{\frac{1}{2}} \geqslant 48$ h) at atmospheric pressure of CO.

(*c*) *The* X-*Ray Structures of Complexes* (**2**) *and* (**5**).—Interatomic distances in complexes (**2**) and (**5a**) are given in Tables 1 and 2 respectively. The molecular structure of (**5a**) (Figure 1) should be contrasted with that of (**3**).[13] In (**5a**) there are two short (mean 2.679 Å) and one long (2.816 Å) Ru–Ru bonds. The hydrogen atom bridges the long Ru–Ru bond. The Ru–Ru distances in (**3**) for the two long and one short bonds are 2.805(1) (mean) and 2.680(1) Å respectively. The two hydrogen atoms bridge the two long Ru–Ru bonds.[13] The average Ru–N distances in complexes (**1**), (**3**), (**5a**), and $[Ru_3(\mu_3\text{-}NPh)(CO)_9I]^-$ are very similar, 2.055, 2.068, 2.073, and 2.062 Å respectively.

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* The homogeneity of these systems have been established by performing the Collman test (J. P. Collman, K. M. Kosydar, M. Bressan, W. Lamanna, and T. Garrett, *J. Am. Chem. Soc.*, 1984, **106**, 2569). Both soluble and cross-linked nitropolystyrene can be reduced and carbonylated by the catalytic systems discussed in this work (see Experimental section).

† Geoffroy and co-workers have developed a further improved and general method of synthesis involving reaction of cluster carbonyls in acetonitrile with trimethylamine oxide, followed by nitrosobenzene (G. L. Geoffroy, personal communication).

Table 1. Bond lengths (Å) in complex (**2**)

Ru(1)–Ru(2)	2.826(1)	Ru(1)–Ru(3)	2.767(1)
Ru(1)–C(11)	1.925(3)	Ru(1)–C(12)	1.904(3)
Ru(1)–C(13)	1.902(3)	Ru(1)–N	2.140(2)
Ru(2)–Ru(3)	2.838(1)	Ru(2)–C(21)	1.936(3)
Ru(2)–C(22)	1.933(4)	Ru(2)–C(23)	1.928(3)
Ru(2)–C(24)	1.937(3)	Ru(3)–C(31)	1.941(4)
Ru(3)–C(32)	1.903(3)	Ru(3)–C(33)	1.892(3)
Ru(3)–N	2.130(2)	H(1)–Ru(1)	1.80(3)
H(1)–Ru(3)	1.86(3)	C(1)–C(2)	1.384(4)
C(1)–C(6)	1.397(4)	C(1)–N	1.434(3)
C(2)–C(3)	1.383(5)	C(3)–C(4)	1.394(6)
C(4)–C(5)	1.371(6)	C(5)–C(6)	1.388(4)
C(11)–O(11)	1.133(3)	C(12)–O(12)	1.128(4)
C(13)–O(13)	1.132(4)	C(21)–O(21)	1.131(4)
C(22)–O(22)	1.121(4)	C(23)–O(23)	1.128(4)
C(24)–O(24)	1.118(4)	C(31)–O(31)	1.124(4)
C(32)–O(32)	1.122(4)	C(33)–O(33)	1.133(4)

Table 2. Bond lengths (Å) in complex (**5a**)

Ru(1)–Ru(2)	2.686(2)	Ru(1)–Ru(3)	2.673(2)
Ru(1)–C(11)	1.894(12)	Ru(1)–C(12)	1.913(11)
Ru(1)–C(13)	1.934(11)	Ru(1)–N(1)	2.062(8)
Ru(2)–Ru(3)	2.816(2)	Ru(2)–C(21)	1.894(12)
Ru(2)–C(22)	1.952(11)	Ru(2)–C(23)	1.930(13)
Ru(2)–N(1)	2.087(9)	Ru(3)–C(31)	1.892(13)
Ru(3)–C(32)	1.920(11)	Ru(3)–C(33)	1.922(12)
Ru(3)–N(1)	2.071(9)	C(11)–O(11)	1.139(15)
C(12)–O(12)	1.118(15)	C(13)–O(13)	1.136(15)
C(21)–O(21)	1.136(15)	C(22)–O(22)	1.102(14)
C(23)–O(23)	1.117(16)	C(31)–O(31)	1.129(16)
C(32)–O(32)	1.154(14)	C(33)–O(33)	1.112(15)
C(41)–C(42)	1.343(17)	C(41)–C(46)	1.376(16)
C(41)–N(1)	1.408(14)	C(42)–C(43)	1.414(19)
C(43)–C(44)	1.389(20)	C(44)–C(45)	1.394(21)
C(45)–C(46)	1.398(20)	C(511)–P(1)	1.792(8)
C(521)–P(1)	1.787(8)	C(531)–P(1)	1.792(8)
C(611)–P(2)	1.773(7)	C(621)–P(2)	1.780(8)
C(631)–P(2)	1.790(7)	N(2)–P(1)	1.575(10)
N(2)–P(2)	1.574(10)		

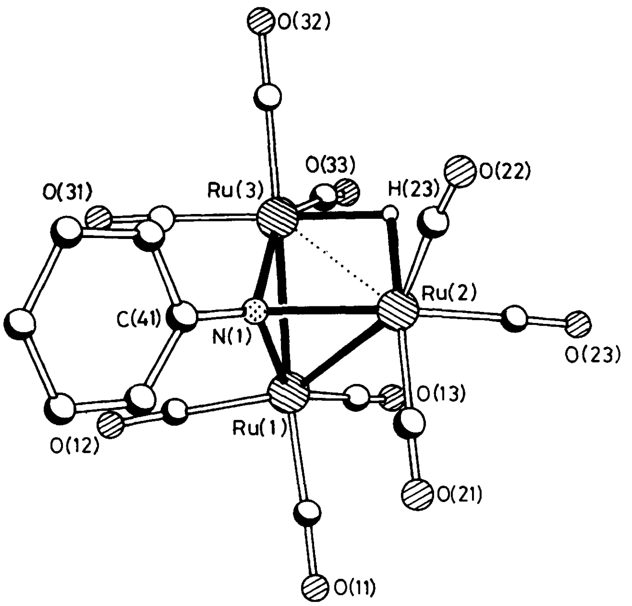


Figure 1. Molecular structure of complex (**5a**) showing the atom numbering scheme. Radii arbitrary, H atoms of the benzene ring not shown. The long Ru–Ru bond is indicated by a dotted line

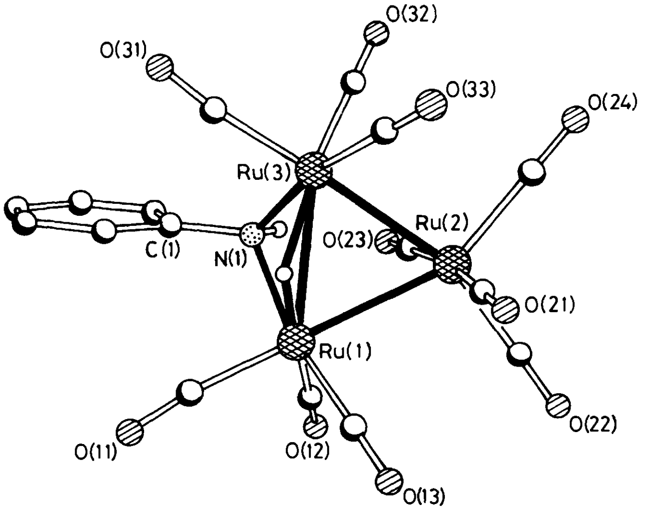


Figure 2. Molecular structure of complex (**2**) showing the atom numbering scheme. Radii arbitrary, H atoms of the benzene ring not shown

There are however two important differences between the structure of (**5a**) and that of the iodide analogue.[9] First, whereas in (**5a**) all the nine carbonyl groups are terminal, the iodide complex contains a unique CO group that caps the three ruthenium atoms asymmetrically. Secondly, whereas the iodide adopts a terminal position, the hydride is considered to bridge the long Ru(2)–Ru(3) bond.

The molecular structure of complex (**2**) (Figure 2) is similar to that of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PhCH_2NH)]$ reported by Lausarot *et al.*[18] Both these complexes have two long and one short Ru–Ru bonds, the latter being bridged by the amido groups and the hydride. The mean long Ru–Ru distance in (**2**) and the benzyl analogue are 2.832(1) and 2.828(2) Å, whereas the short Ru–Ru bonds are 2.767(1) and 2.746(2) Å respectively. The average Ru–N distances, 2.135(2) in (**2**) and 2.096(5) Å in the benzyl derivative, are also similar.

(*d*) *Reactions of Complexes* (**2**) *and* (**3**).—Reactions of complexes (**2**) and (**3**) with methanolic KOH leading to the formation of (**4**) and (**5**) respectively have already been mentioned. We find that (**2**) and (**3**) can be interconverted *via* decarbonylation and carbonylation. The conditions, 108 °C for (**2**) into (**3**) and 80 °C, 120 lbf in^{-2} CO for (**3**) into (**2**), required for these transformations are well within the ranges used for effecting catalytic reduction of $PhNO_2$ to $PhNH_2$ in the absence of OH^- ions (see Experimental section). A similar reversible relationship between the benzyl analogues of (**2**) and (**3**) has recently been reported by Vahrenkamp and co-workers.[19] The relatively facile interconversion of (**2**) and (**3**) should be contrasted with their osmium analogues, where decarbonylation of the amide complex results mainly in orthometallation.[20] However, facile decarbonylation of a triosmium cluster with a doubly bridging methylamido group, leading to the formation of a μ_3-NMe ligand, has also been reported.[16a].

Both complexes (**2**) and (**3**) react with hydrogen (110 °C, 300 lbf in^{-2}) to give $[Ru_4H_4(CO)_{12}]$ and aniline; $[Ru_4H_4(CO)_{12}]$ in turn reacts with $PhNO_2$ in the presence of CO (110 °C, 200 lbf in^{-2}) to give CO_2 and a mixture of $[Ru_3(CO)_{12}]$ and (**3**). This suggests stoicheiometries as shown in equations (1) and (2) for

$$4[Ru_3H(CO)_{10}(PhNH)] + 6H_2 \longrightarrow 3[Ru_4H_4(CO)_{12}] + 4PhNH_2 + 4CO \quad (1)$$

$$4[Ru_3H_2(CO)_9(PhN)] + 6H_2 \longrightarrow 3[Ru_4H_4(CO)_{12}] + 4PhNH_2 \quad (2)$$

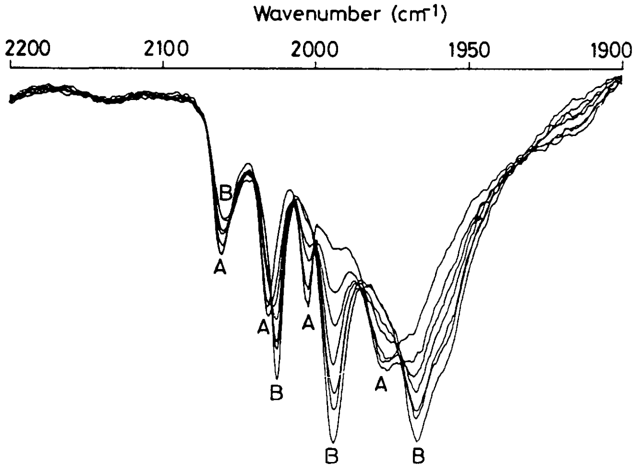


Figure 3. Conversion of complex (**4**) into (**5a**) monitored by i.r. spectroscopy. Bands A and B refer to (**4**) and (**5a**) respectively

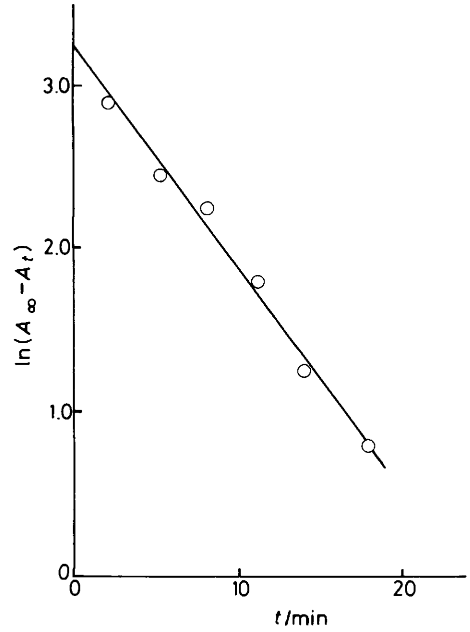


Figure 4. Plot of $\ln(A_\infty - A_t)$ *vs.* time at 55 °C for the conversion of complex (**4**) into (**5a**). The absorbance is measured at 1 995 cm^{-1}

the first two reactions. Formation of $[Ru_3(CO)_{12}]$ from (**3**) under CO pressure is a known reaction.[13]

(*e*) *Reactivities of Complexes* (**4**)—(**6**).—Under ambient conditions in solution complex (**4**) undergoes slow CO loss to give (**5**). However, the reverse reaction, *viz.* carbonylation of (**5**) to (**4**), cannot be achieved even with moderately high ($\leqslant 800$ lbf in^{-2}) pressure of CO. At temperatures below 30 °C no reaction of (**5**) with CO is observed up to a pressure of 300 lbf in^{-2}, when there is spectroscopic evidence for the formation of a new species formulated as $[Ru_3(CO)_{10}(PhNH)]^-$ (**7**). Attempts to isolate (**7**) in the solid state result in decarbonylation and (**5**) is obtained quantitatively. The treatment of (**7**) with non-co-ordinating acids leads mainly to a mixture of (**2**) and (**3**) with traces of $[Ru_3(CO)_{12}]$. On carbonylation the migration of a hydrogen atom from the metal framework to the capping μ_3-NPh ligand is thus observed with both the neutral complex (**3**) and its anionic derivative (**5**). Facile loss of CO accompanied by the migration of a hydrogen atom from the metal framework to the nitrogen has also been observed in the osmium 'isocyanate' complex reported by Deeming *et al.*[17]

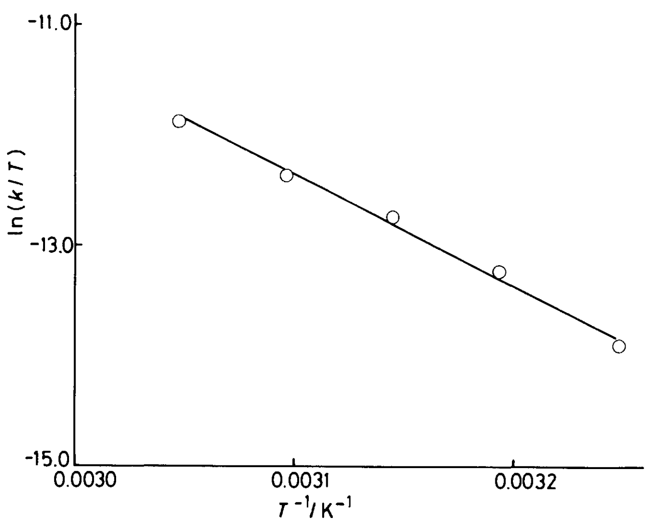


Figure 5. Plot of $\ln(k/T)$ *vs.* $1/T$ for the conversion of complex (**4**) into (**5a**)

As already mentioned, carbonylation of complex (**4**) leading to the formation of (**6**) is exceedingly slow under atmospheric pressure of CO. However, carbonylation at ambient temperature under elevated pressure ($\geqslant 80$ lbf in^{-2}) results in migration of the hydrogen atom from the metal framework to the carbon atom of the isocyanate function. At higher temperatures (80 °C, 350 lbf in^{-2} CO) both (**4**) and (**5**) give PhNCO, but we have so far not been able to characterise the organometallic residues obtained from these reactions. Two points, both of direct relevance to catalytic systems involving OR^- as the promoter, should be noted. First, $[Ru_3H(CO)_{11}]^-$, a species that could be expected to arise in the reaction of (**4**) or (**5**) with CO, is not detected. Secondly, in separate experiments it was found that reactions of $[Ru_3H(CO)_{11}]^-$ with PhNO or $PhNO_2$ lead to the formation of a mixture of (**4**) and (**5**) in low yields.

Whereas the treatment of complex (**5**) with non-co-ordinating acids leads quantitatively to (**3**), a mixture of (**2**), (**3**), and $[Ru_4H_4(CO)_{12}]$ is obtained from (**4**) under similar conditions. Reactions of (**4**)—(**6**) with water or methanol at temperatures $\leqslant 68$ °C under an atmosphere of CO have also been studied, because these are the conditions used in the catalytic system involving $[Ru_3(CO)_{12}]$ as the precatalyst and OH^- or OMe^- ions as promoters. Trace ($\leqslant 5\%$) quantities of complex (**3**) are formed in the reaction between (**5**) and water or methanol. Most of the anionic complex is recovered unchanged. However, both (**6**) and (**4**) react with water ($t_{\frac{1}{2}} \approx 2$ h) to give formanilide and aniline respectively as the major ($\geqslant 80\%$) organic products, accompanied by $[Ru_3(CO)_{12}]$. Under similar conditions reaction of (**6**) with methanol also leads to the formation of formanilide and $[Ru_3(CO)_{12}]$. These observations are rationalised according to equations (3) and (4).

$$(\mathbf{6}) + 2CO + ROH \xrightarrow{R\,=\,Me\text{ or }H} [Ru_3(CO)_{12}] + PhNHCHO + OR^- \quad (3)$$

$$(\mathbf{4}) + 2CO + H_2O \longrightarrow [Ru_3(CO)_{12}] + PhNH_2 + OH^- \quad (4)$$

(*f*) *Kinetic Studies on the Conversion of Complex* (**4**) *into* (**5**).—The loss of CO by complex (**4**) to give (**5**) can be monitored by i.r. spectroscopy (Figure 3) Plots of $\ln(A_\infty - A_t)$ against time (Figure 4) are linear, indicating that the reaction is first order with respect to the concentration of (**4**). Measurement of the rate constant at five different temperatures and a plot of $\ln(k/T)$ against $1/T$ (Figure 5) gives the 95% confidence-limit

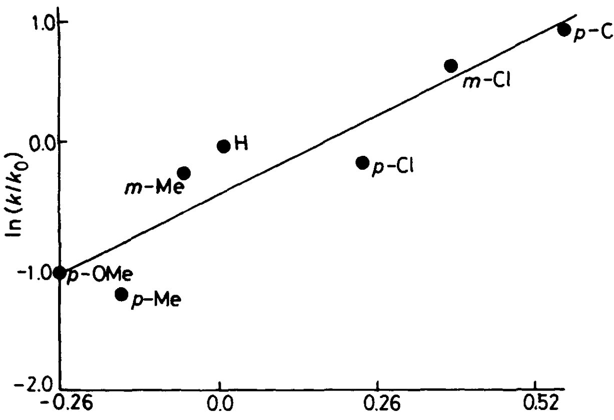
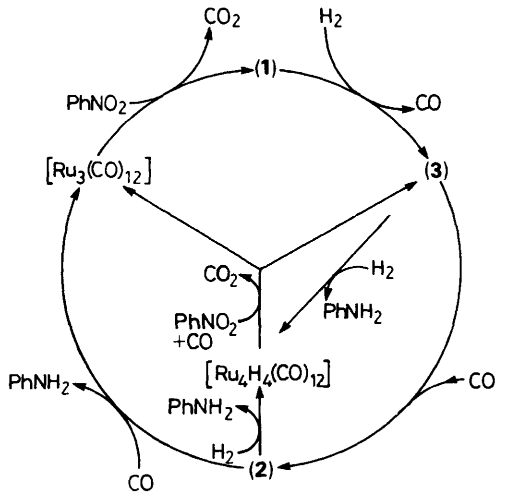
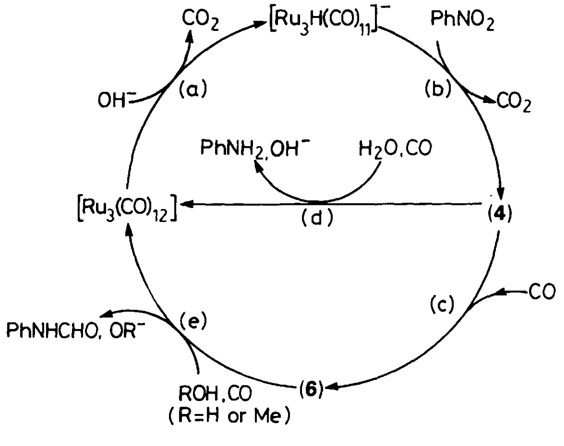


Figure 6. Hammett plot for the conversion of complex (**4**) into (**5a**)



Scheme 2.



Scheme 3.

values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as -20.8 ± 3.4 kcal mol^{-1} and -7.4 ± 10.8 cal K^{-1} mol^{-1} respectively.

A plausible mechanism for the conversion of complex (**4**) into (**5**) involves loss of CO from the bound PhNCO moiety accompanied by accumulation of negative charge on the nitrogen atom, followed by the formation of the third Ru–N bond. To test the validity of such a hypothesis, a Hammett plot of the conversion of (**4**) into (**5**) was attempted. By using substituted anilines, analogues of (**2**) and (**4**) were easily made and kinetic studies were performed on the conversion of the isocyanato clusters into the μ_3-NPh clusters. As shown in Figure 6, although there is a noticeable scatter in the resultant Hammett plot, σ and $\ln(k/k_0)$ appear to be linearly related. In other words the slope is positive although there is some uncertainty in its precise value. While too much importance should not be attached to it, the least-squares-fitted straight line has a slope (ρ) of +2.5. The positive slope indicates a transition state where negative charge is accumulated on the aromatic ring. This is consistent with the above mechanism.

(*g*) *Models for Catalytic Cycles.*—Based on the reactions of complexes (**1**)—(**6**) described above, two hypothetical models for the catalytic reductions of nitrobenzene to aniline may be proposed. As shown in Scheme 2, the first cycle rationalises formation of aniline where either a mixture of CO and H_2 or only CO in the presence of a protic solvent are used as the reductants. Part of this catalytic cycle,[13] excluding participation by (**2**) and $[Ru_4H_4(CO)_{12}]$, was proposed by us in 1984. It is well known[21] that, in the presence of protic solvents or under high pressures of hydrogen, $[Ru_4H_4(CO)_{12}]$ is easily formed. It should be noted that $[Ru_4H_4(CO)_{12}]$ has also been found to be an active precatalyst.

One obvious shortcoming of the hypothetical cycle is that it does not include the pathways by which $[Ru_3(CO)_{12}]$ is degraded. Under the conditions employed by us (see Experimental section) the recovery of $[Ru_3(CO)_{12}]$ at the end of any particular run is never more than 10%. The rest of the ruthenium-containing residue is soluble in organic solvents such as methanol and dichloromethane, contains i.r. bands indicative of the presence of carbonyls, but has so far eluded separation and characterisation by chromatographic methods and/or fractional crystallisation.

Scheme 3 may be proposed for reactions where OH^- or OMe^- ions are used as promoters, and CO is used at atmospheric pressure. Complexes (**4**) and (**6**) rather than (**5**) seem to be important catalytic intermediates since they are capable of regenerating $[Ru_3(CO)_{12}]$ by their reaction with water or methanol [see reactions (3) and (4)]. Furthermore the reaction of PhNO or $PhNO_2$ with $[Ru_3H(CO)_{11}]^-$, a cluster known to be formed in the reaction of OH^- with $[Ru_3(CO)_{12}]$,[22] leads to the formation of (**5**) and (**4**). Since step (d) is considerably faster than (c), aniline is obtained quantitatively in the presence of large quantities of water. Under reaction conditions where only trace quantities of water are present, step (d) is avoided to a considerable extent and formanilide is obtained as the major product. It is reasonable to assume that under these conditions catalytic quantities of $[Ru_3H(CO)_{11}]^-$ are formed.

Finally it should be pointed out that Schemes 2 and 3 are proposed as hypothetical models that consist of reactions of fully characterised species. Obviously these reactions do not rule out the existence of other pathways involving transient cluster or mononuclear intermediates that have not been detected so far.

Experimental

General Comments.—All manipulations were carried out under a dry dinitrogen atmosphere by using standard Schlenk and syringe techniques unless otherwise stated.[23] Solvents were distilled from the appropriate drying agents before use.[24] The compounds $[Ru_3(CO)_{12}]$,[25] $[Ru_4H_4(CO)_{12}]$,[21] $[Ru_3H(CO)_{10}(PhNH)]$,[14] $[Ru_3H(CO)_{11}]^-$,[26] and $[N(PPh_3)_2]Cl$[27] were prepared according to literature procedures. Infra-red and n.m.r. spectra were recorded on a PE 781 and a Bruker 80-MHz Fourier-transform instrument. Gas chromatographic analyses were performed on a Shimadzu GC 9A with a 30-m capillary

Table 3. Characterisation data for analogues of (**2**) and (**4**)

	Analogue of (**2**)			Analogue of (**4**)				
						Analyses/%		
Substituent	I.r. (cm^{-1})^a	^{1}H N.m.r. (δ)^b	M^c	I.r. (cm^{-1})^d	^{1}H N.m.r. (δ)^b	C	H	N
p-OMe	2 100m, 2 065vs, 2 051vs, 2 026vs, 2 011vs, 2 003vs (sh), 1 981m	7(m), 6.2(s), 3.75(s), −12.7(d)	786	2 062m, 2 032vs, 2 004vs, 1 978vs, 1 610m	7(m), 3.75(s), −14(s)	52.2 (51.7)	3.80 (3.85)	2.30 (2.25)
p-Me	2 100m, 2 064vs, 2 051vs, 2 026vs, 2 011vs, 2 004vs (sh), 1 981m	7(m), 6.2(s), 2.2(s), −12.7(d)	698	2 060m, 2 030vs, 2 003vs, 1 980vs, 1 612m	7(m), 2.2(s), −14(s)	51.50 (51.85)	3.10 (3.10)	2.10 (2.30)
m-Me	2 100m, 2 065vs, 2 052vs, 2 026vs, 2 011vs, 2 004vs (sh), 1 982m	7(m), 6.1(s), 2.2(s), −12.7(d)	698	2 064m, 2 032vs, 2 004vs, 1 979vs, 1 610m	7(m), 2.2(s), −13.9(s)	52.00 (51.85)	3.30 (3.10)	2.15 (2.30)
p-Cl	2 104m, 2 066vs, 2 054vs, 2 026vs, 2 012vs, 2 004vs (sh), 1 982m	7(m), 6.0(s), −12.7(d)	710	2 062m, 2 031vs, 2 004vs, 1 978vs, 1 610m	7(m), −14.1(s)	50.50 (50.00)	2.80 (2.80)	2.20 (2.25)
m-Cl	2 102m, 2 065vs, 2 054vs, 2 026vs, 2 012vs, 2 004vs (sh), 1 982m	7(m), 5.9(s), −12.8(d)	710	2 062m, 2 032vs, 2 004vs, 1 980vs, 1 608m	7(m), −14.1(s)	50.10 (50.00)	2.75 (2.80)	2.20 (2.25)
p-CF_3	2 102m, 2 066vs, 2 054vs, 2 026vs, 2 012vs, 2 004vs (sh), 1 982m	7(m), 6.8(s), −12.7(d)	744	2 062m, 2 032vs, 2 004vs, 1 978vs, 1 610m	7(m), −14(s)	49.60 (49.65)	2.60 (2.75)	2.20 (2.20)

[a] In n-hexane. [b] In $CDCl_3$. [c] *m*/*z*. [d] In CH_2Cl_2. [e] Calculated values are given in parentheses.

Table 4. Details of data collection and structure refinement

Compound	(**2**)	(**5a**)
Formula	$C_{16}H_7NO_{10}Ru_3$	$C_{51}H_{36}N_2O_9P_2Ru_3$
M	676.4	1 186.0
Space group	$P\bar{1}$	$P2_1/c$
a/Å	8.575(2)	10.876(3)
b/Å	9.460(2)	16.553(4)
c/Å	13.114(2)	27.894(7)
α/°	98.79(2)	90
β/°	92.02(3)	96.87(2)
γ/°	94.98(2)	90
U/Å^3	1 046.0	4 985.9
Z	2	4
D_c/g cm^{-3}	2.15	1.58
F(000)	644	2 360
μ/mm^{-1}	2.1	1.0
Crystal size (mm) habit	0.6 × 0.3 × 0.1, orange prism	0.45 × 0.1 × 0.08, yellow needle
Transmission factors	0.69—0.99	0.75—0.78
$2\theta_{max.}$/°	60	45
Reflections		
measured	6 106	6 891
unique	6 088	6 484
(R_{int})	(0.016)	(0.029)
observed	5 275 [$F > 4\sigma(F)$]	4 290 [$F > 3\sigma(F)$]
R	0.030	0.082
R'	0.030	0.062
G	0.000 25	0.000 25
Parameters	280	307
S	1.4	1.5
Maximum shift/e.s.d.	0.003	0.002
Maximum electro-density/e Å^{-3}	0.65	1.34

Table 5. Atomic co-ordinates (× 10^4) for complex (**2**)

Atom	x	y	z
Ru(1)	7 234.3(2)	3 754.0(2)	3 212.7(1)
Ru(2)	4 893.9(3)	4 315.2(2)	1 795.4(2)
Ru(3)	4 745.2(2)	1 697.2(2)	2 609.7(2)
H(1)	5 626(34)	2 875(32)	3 798(21)
C(1)	8 136(3)	599(3)	2 519(2)
C(2)	9 040(4)	−38(3)	1 757(3)
C(3)	10 022(4)	−1 055(4)	1 964(3)
C(4)	10 088(5)	−1 450(4)	2 945(4)
C(5)	9 184(4)	−842(4)	3 704(3)
C(6)	8 205(4)	184(3)	3 496(3)
C(11)	8 610(3)	3 383(3)	4 314(2)
C(12)	8 853(4)	4 613(3)	2 488(2)
C(13)	6 842(3)	5 542(3)	3 995(2)
C(21)	3 778(4)	5 041(3)	2 994(2)
C(22)	5 544(4)	6 262(4)	1 605(2)
C(23)	6 283(4)	3 501(3)	787(2)
C(24)	3 014(4)	3 877(4)	899(3)
C(31)	4 606(4)	27(4)	3 308(3)
C(32)	3 919(4)	736(4)	1 295(3)
C(33)	2 722(3)	2 118(3)	3 022(3)
N	7 161(3)	1 678(2)	2 288(2)
H(1N)	7 284(32)	1 770(30)	1 637(21)
O(11)	9 442(3)	3 329(3)	4 994(2)
O(12)	9 834(3)	5 085(3)	2 057(2)
O(13)	6 632(3)	6 601(3)	4 476(2)
O(21)	3 104(3)	5 513(3)	3 670(2)
O(22)	5 887(4)	7 403(3)	1 508(2)
O(23)	7 102(3)	3 061(3)	189(2)
O(24)	1 931(3)	3 600(4)	382(2)
O(31)	4 352(4)	−945(3)	3 693(3)
O(32)	3 412(4)	177(3)	523(2)
O(33)	1 510(3)	2 353(3)	3 278(2)

column of silica under isothermal (150 °C) conditions with a flame ionisation detector. For some experiments, temperature-programmed gas chromatographic analyses were carried out on a HP 5890 A instrument. A Carlo-Erba 1106 instrument was used for microanalyses. Mass spectra were recorded on a A.E.I. M.S. 12 spectrometer using tris(perfluoroheptyl)-1,3,5-triazine as calibrant. High-pressure experiments were carried out in Parr bench-top 'Mini' reactors 4565 and 4561.

Carbon monoxide was dried by carrying out two reactions in series. Typically a catalytic run was first carried out in a reactor (300 cm^3) under specified conditions. This reactor was then cooled (0 °C) and connected to another reactor (100 cm^3). The CO from the first reactor was then used to purge and pressurise

Table 6. Atomic co-ordinates (× 10^4) for complex (**5a**)

Atom	*x*	*y*	*z*
Ru(1)	506(1)	1 203.2(6)	1 546.4(3)
Ru(2)	549(1)	1 834.3(6)	2 435.5(3)
Ru(3)	379(1)	157.8(6)	2 269.1(3)
C(11)	918(11)	2 140(7)	1 210(4)
C(12)	1 143(11)	463(7)	1 111(4)
C(13)	−1 230(11)	1 204(7)	1 295(4)
C(21)	1 342(11)	2 767(7)	2 226(4)
C(22)	1 173(11)	1 972(7)	3 116(4)
C(23)	−1 060(12)	2 325(8)	2 436(4)
C(31)	995(12)	−718(7)	1 933(4)
C(32)	781(11)	−336(7)	2 891(4)
C(33)	−1 287(11)	−227(7)	2 111(4)
C(41)	3 025(10)	964(6)	2 241(4)
C(42)	3 740(11)	1 292(8)	1 932(5)
C(43)	5 047(13)	1 240(9)	2 009(5)
C(44)	5 634(13)	828(8)	2 406(5)
C(45)	4 908(12)	487(9)	2 733(5)
C(46)	3 623(14)	569(8)	2 636(5)
C(512)	4 223(6)	3 337(5)	866(3)
C(513)	4 466	3 478	1 362
C(514)	5 664	3 383	1 596
C(515)	6 620	3 145	1 335
C(516)	6 377	3 004	839
C(511)	5 179	3 100	605
C(522)	2 472(7)	3 381(4)	−282(3)
C(523)	1 580	3 924	−489
C(524)	1 941	4 625	−711
C(525)	3 196	4 783	−728
C(526)	4 088	4 241	−521
C(521)	3 726	3 540	−299
C(532)	3 796(7)	1 592(5)	−550(2)
C(533)	3 361	801	−607
C(534)	3 385	293	−207
C(535)	3 845	577	251
C(536)	4 280	1 368	308
C(531)	4 256	1 875	−92
C(612)	6 249(6)	1 490(4)	−1 266(3)
C(613)	5 562	1 104	−1 654
C(614)	4 692	1 539	−1 960
C(615)	4 507	2 358	−1 876
C(616)	5 194	2 744	−1 488
C(611)	6 065	2 309	−1 182
C(622)	9 253(7)	2 214(4)	−745(2)
C(623)	10 286	1 740	−592
C(624)	10 291	1 253	−184
C(625)	9 264	1 241	72
C(626)	8 232	1 716	−81
C(621)	8 226	2 203	−490
C(632)	7 692(7)	3 849(4)	−1 370(2)
C(633)	8 206	4 571	−1 510
C(634)	8 489	5 186	−1 172
C(635)	8 528	5 078	−695
C(636)	7 744	4 356	−556
C(631)	7 461	3 741	−893
N(1)	1 723(9)	1 001(5)	2 160(3)
N(2)	6 166(8)	2 979(5)	−241(3)
O(11)	1 151(10)	2 681(6)	985(3)
O(12)	1 533(9)	43(5)	854(3)
O(13)	−2 251(9)	1 179(6)	1 151(3)
O(21)	1 812(9)	3 333(5)	2 107(3)
O(22)	1 500(11)	2 090(7)	3 499(3)
O(23)	−2 003(9)	2 596(6)	2 424(4)
O(31)	1 304(10)	−1 250(6)	1 725(3)
O(32)	993(9)	−678(6)	3 252(3)
O(33)	−2 236(9)	−434(7)	1 972(4)
P(1)	4 899(3)	2 872(2)	−27(1)
P(2)	6 902(3)	2 804(2)	−682(1)

the second reactor. Kinetic experiments were carried out by taking solutions of complex (**4**) (6 mg, 0.005 mmol) in tetrahydrofuran (2 cm^3) in a double-jacketed vessel. Water at constant temperature (± 0.2 °C) was circulated through the outer jacket and the changes in the i.r. spectra were monitored with time. The changes in the absorbance near 1 995 cm^{-1} were used in the plots of $\ln(A_\infty - A_t)$ *vs.* time. The slopes of the resultant straight lines were calculated by the least-squares method. The activation parameters were determined from a plot of $\ln(k/T)$ *vs.* $1/T$ using rate constants determined at 35, 40, 45, 50, and 55 °C. The 95% confidence limits were calculated according to well established procedures.[28] The data used for the characterisation of the analogues of (**2**) and (**4**) with substituted anilines are given in Table 3. They were prepared by the same methods employed for (**2**) and (**4**).

Crystal Structure Determinations.—Intensities were measured on a Stoe-Siemens four-circle diffractometer in profile-fitting mode,[29] using monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Cell constants were refined from *ca.* 40 selected strong reflections in the range 2θ 20—30°. Absorption corrections based on ψ scans were applied.

Structures were solved by the heavy-atom method and subjected to full-matrix refinement on *F*. For compound (**2**) all non-hydrogen atoms were refined anisotropically, aromatic H included using a riding model, cluster hydride and NH (both clearly identified in difference syntheses) refined freely. An extinction correction of the form $F_{corr} = F_c/(1 + xF_c^2/\sin 2\theta)^{0.25}$ was applied, where *x* refined to 5.6(3) × 10^{-6}.

For compound (**5a**) only the Ru, P, N, and O atoms and the C atoms of the PhN group were refined anisotropically; the phenyl groups of the cation were refined as rigid groups with C–C 1.395 and C–H 0.96 Å, all angles 120°. The cluster hydride was not located crystallographically, but its position was calculated from potential-energy considerations[30] and it was held fixed at this position (Ru–H 1.803 Å). A weighting scheme of the form $w^{-1} = \sigma^2(F) + gF^2$ were used. The program system was SHELX 76, locally modified by its author G. M. Sheldrick.

All other details of the crystal data, data collection, and refinement are given in Table 4. The atomic co-ordinates for (**2**) and (**5a**) are given in Tables 5 and 6 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and bond angles.

Catalytic Experiments.—(*a*) *Reaction of* $PhNO_2$ *with* CO. In a reactor (300 cm^3) were placed $[Ru_3(CO)_{12}]$ (64 mg, 0.1 mmol) and $PhNO_2$ (620 mg, 5.0 mmol). Freshly distilled dry MeCN (30 cm^3) was added under dry nitrogen; the reactor was then pressurised with CO (640 lbf in^{-2}) from the cylinder and the reaction continued at 160 °C for 20 h. Gas chromatographic anslysis of the solution showed conversion into PhNCO (5%) and $PhNH_2$ (40%). The compound $(PhNH)_2CO$ ($\approx$120 mg) was obtained as a microcrystalline white solid, identified from its spectroscopic data. Use of not freshly distilled MeCN gave PhNCO (3%), $PhNH_2$ (55%), and $(PhNH)_2CO$ (80 mg).

In the follow-up experiment, a reactor (100 cm^3) containing $[Ru_3(CO)_{12}]$ (64 mg, 0.1 mmol), $PhNO_2$ (620 mg, 5.0 mmol), and dry MeCN (30 cm^3) was first purged and then pressurised with CO (400 lbf in^{-2}) from the cooled (0 °C) 300-cm^3 reactor. The 100-cm^3 reactor was then heated at 160 °C and the reaction continued for 20 h. Gas chromatographic analysis of the solution showed conversion into PhNCO (32%) and $PhNH_2$ (3%).

(*b*) *Reaction of* $PhNO_2$ *with* CO *and* H_2. A reactor (100 cm^3) containing $[Ru_3(CO)_{12}]$ (64 mg, 0.1 mmol), $PhNO_2$ (620 mg, 5.0 mmol), and dry heptane (30 cm^3) was pressurised with a 1:1 mixture of CO and H_2 at 600 lbf in^{-2}. It was heated at 120 °C and reaction was carried out for 10 h. Analysis of the solution by g.c. showed 40% conversion into aniline only. Under the same conditions in acetonitrile there was complete conversion into aniline. In both cases the solid residues obtained by taking the solutions to dryness were subjected to t.l.c. Recovery of $[Ru_3(CO)_{12}]$ was about 10%. The reaction with $[Ru_4H_4(CO)_{12}]$ (74 mg, 0.1 mmol) as a catalyst was carried out in a similar fashion and gave similar results.

(*c*) *Reaction of* $PhNO_2$ *with* CO *and* Me_2CHOH. A reactor (100 cm^3) containing $[Ru_3(CO)_{12}]$ (64 mg, 0.1 mmol), $PhNO_2$ (620 mg, 5.0 mmol), and isopropyl alcohol (30 cm^3) was pressurised with CO at 600 lbf in^{-2}. It was heated at 120 °C and reaction was carried out for 16 h. Analysis of the solution by g.c. showed 60% conversion into aniline (50%) and isopropyl(phenyl)amine (10%). Acetone, corresponding to an approximately 40% conversion of nitrobenzene, was also detected by g.c. Recovery of $[Ru_3(CO)_{12}]$ by t.l.c. was about 5%. The reaction with $[Ru_4H_4(CO)_{12}]$ (74 mg, 0.1 mmol) as a catalyst was carried out in a similar fashion, and similar results were obtained.

(*d*) *Reaction of nitropolystyrene with* $[Ru_3(CO)_{12}]$ *as the precatalyst.* Soluble and 8% divinylbenzene cross-linked polystyrene (5 g) was nitrated with fuming nitric acid (100 cm^3) at room temperature over a period of 10 h. The catalytic experiments under the same experimental conditions as described in (*a*)—(*c*) were carried out with 1 g nitropolystyrene substrates. Disappearance of i.r. bands at 1 560 and 1 350 cm^{-1} was taken to be indicative of reaction on the nitro group. Formation of NCO, $(NH)_2CO$, and $NHCO_2Me$ functionalities was indicated by i.r. bands at 2 250, 1 660, and 1 720 cm^{-1} respectively.

Synthesis of $[N(PPh_3)_2][Ru_3H(CO)_9(PhNCO)]$ (**4**). To a suspension of complex (**2**) (37 mg, 0.054 mmol) in methanol (5 cm^3) was added KOH (3.7 mg, 0.065 mmol) dissolved in methanol (1 cm^3). The mixture was stirred for 10 min until the solid dissolved and then $[N(PPh_3)_2]Cl$ (31 mg, 0.054 mmol) in methanol (1 cm^3) was added. After stirring for 2 min, the clear orange solution was taken to dryness under vacuum and the residue washed thoroughly with hexane. It was then extracted with diethyl ether, which on concentration gave yellow crystals of complex (**4**). Yield = 45 mg (69%) (Found: C, 50.9; H, 3.15; N, 2.20. Calc. for $C_{52}H_{36}N_2O_{10}P_2Ru_3$; C, 51.15; H, 2.95; N, 2.30%). I.r. (ν_{CO}, CH_2Cl_2); 2 066m, 2 034vs, 2 006vs, 1 980vs, br, and 1 610m cm^{-1}. ^1H N.m.r. (CD_2Cl_2, 30 °C): δ −14.0(s).

Synthesis of $[N(PPh_3)_2][Ru_3H(CO)_9(PhN)]$ (**5**). To a suspension of complex (**3**) (40 mg, 0.062 mmol) in methanol (5 cm^3) was added KOH (4.2 mg, 0.074 mmol) dissolved in methanol (1 cm^3). The mixture was stirred for 1 h, when a clear yellow solution was obtained. To this was added $[N(PPh_3)_2]Cl$ (190 mg, 0.330 mmol) in methanol (2 cm^3). After stirring for 2 min the solution was concentrated under vacuum and left at 0 °C for 16 h. Crystals thus obtained were washed thoroughly with hexane and then extracted with diethyl ether, which on concentration gave yellow crystals of complex (**5**). Yield = 55 mg (75%) (Found: C, 51.30; H, 3.10; N, 2.25. Calc. for $C_{51}H_{36}N_2O_9P_2Ru_3$; C, 51.65; H, 3.05; N, 2.35%). I.r (ν_{CO}, CH_2Cl_2); 2 054w, 2 026s, 1 994vs, 1 966s, br, and 1 915w (sh), cm^{-1}. ^1H N.mr. (CD_2Cl_2, 30 °C): δ −16.30(s).

Reaction of complex (**1**) *with* $NaBH_4$ *in tetrahydrofuran* (*thf*). To a thf solution (10 cm^3) containing complex (**1**) (35 mg, 0.051 mmol) was added solid $NaBH_4$ (5 mg, 0.131 mmol) and the solution stirred for 30 min. The turbid orange-yellow solution was filtered and $[N(PPh_3)_2]Cl$ (30 mg, 0.051 mmol) in CH_2Cl_2 (1 cm^3) was added to the clear filtrate. The solution was taken to dryness and the yellow solid washed with hexane and identified as complex (**5**) on the basis of spectroscopic data.

Synthesis of $[N(PPh_3)_2][Ru_3(CO)_{10}(PhNCHO)]$ (**6**). A solution of complex (**4**) (74.0 mg, 0.061 mmol) in diethyl ether (10 cm^3) was left under 200 lbf in^{-2} CO for 16 h at 27 °C. The solution on concentration gave yellow crystals of (**6**). Yield = 70 mg (92%) (Found: C, 51.00; H, 3.10; N, 2.30. Calc. for $C_{53}H_{36}N_2O_{11}P_2Ru_3$; C, 51.25; H, 2.90; N, 2.25%). I.r (ν_{CO}, CH_2Cl_2); 2 076w, 2 060vw, 2 018s, 1 992vs, br, 1 962m (sh), 1 942m, 1 856vw, and 1 795m, br cm^{-1}. ^1H N.m.r. [in $(CD_3)_2CO$] for $[NBu_4]^+$ salt: δ 6.82 (s, 1 H) and 6.9 (m, 5 H); no Ru–H between δ +10 and −60.

Decarbonylation of complex (**2**) *to give* (**3**). A solution of complex (**2**) (10 mg, 0.014 mmol) in n-heptane (8 cm^3) was heated at 98 °C under argon for 5 h. Monitoring by i.r. spectroscopy showed quantitative conversion of (**2**) into (**3**).

Carbonylation of complex (**3**). A solution of complex (**3**) (40 mg, 0.062 mmol) in hexane (40 cm^3) was placed in a reactor (300 cm^3). The reactor was pressurised with CO at 120 lbf in^{-2} and heated at 80 °C for 6 h. The yellow solution was taken to dryness and then subjected to t.l.c. On elution with hexane three bands corresponding to $[Ru_3(CO)_{12}]$ (3 mg), (**2**) (11 mg), and unreacted (**3**) (12 mg) were obtained. All the compounds were identified by spectroscopic comparisons with authentic samples.

Hydrogenation of complex (**3**). A solution of complex (**3**) (20 mg, 0.031 mmol) in n-heptane (20 cm^3) was placed in a reactor (300 cm^3). The reactor was pressurised with H_2 at 300 lbf in^{-2} and heated at 110 °C for 18 h. At the end of the reaction $[Ru_4H_4(CO)_{12}]$ (18 mg, 0.026 mmol) was recovered from the solution. G.c. analysis of the n-heptane solution confirmed formation of aniline. The reaction between H_2 and complex (**2**) was carried out in a similar fashion.

Reaction of complex (**4**) *with* $HClO_4$ *in* thf. To a solution of complex (**4**) (74.0 mg, 0.061 mmol) in thf (10 cm^3) was added 60% $HClO_4$ (12.0 mg, 0.071 mmol) in thf (1 cm^3). The solution was stirred for 10 min and then taken to dryness. The solid residue was subjected to t.l.c. On elution with hexane three bands corresponding to $[Ru_4H_4(CO)_{12}]$ (10 mg, 0.014 mmol), (**2**) (4 mg, 0.006 mmol), and (**3**) (20 mg, 0.031 mmol) were obtained.

Reaction of complex (**5**) *with* CO: *at ambient temperature.* A solution of complex (**5**) (10 mg, 0.008 mmol) in dichloromethane (10 cm^3) was placed in a reactor (100 cm^3). The reactor was pressurised with CO at 750 lbf in^{-2}. The i.r. spectrum of the solution was taken after 16 h in dichloromethane and bands at 2 060vw, 2 022s, 1 996vs, br, and 1 912vw cm^{-1} were observed. The same experiment when repeated using CD_2Cl_2 and monitored by ^1H n.m.r. spectroscopy showed complete disappearance of the metal hydride signal at δ −16.30. For the $[NBu_4]^+$ salt ^1H n.m.r. signals were observed at δ 7.0 (5 H, m) and 6.7 (1 H, br, s), considered to be due to the NH proton.

Attempts to isolate the solid even under a stream of CO resulted in the formation of complex (**5**) (9 mg, 0.007 mmol).

At 80 °C. A solution of complex (**5**) (15 mg, 0.012 mmol) in dichloromethane (20 cm^3) was placed in a reactor (100 cm^3). The reactor was pressurised with dry CO at 350 lbf in^{-2} and heated at 80 °C for 22 h. The i.r. spectrum of the solution in dichloromethane then showed multiple carbonyl bands. G.c. and gas chromotographic–mass spectrometric (g.c.–m.s.) analyses of the solution established the presence of PhNCO. Aniline was detected when the reaction was carried out under 300 lbf in^{-2} of CO and H_2. The reactions of CO and CO–H_2 with complex (**4**) were carried out in a similar fashion.

Reaction of $[Ru_4H_4(CO)_{12}]$ *with nitrobenzene and* CO. A solution of $[Ru_4H_4(CO)_{12}]$ (37.0 mg, 0.05 mmol) and nitrobenzene (16.0 mg, 0.125 mmol) in n-heptane (40 cm^3) was placed in a reactor (300 cm^3). The reactor was charged with CO at 200 lbf in^{-2} and heated at 110 °C for 4 h. At the end of this period the presence of CO_2 in the vent gas was confirmed by g.c.–m.s. analysis. The solution was taken to dryness and subjected to t.l.c. The complexes $[Ru_3(CO)_{12}]$ (10.0 mg, 0.015 mmol) and (**3**) (20 mg, 0.031 mmol) were isolated and characterised on the basis of spectral data.

Reaction of complex (**5**) *with* $HClO_4$ *in* thf. To a solution of complex (**5**) (71 mg, 0.060 mmol) in thf (10 cm^3) was added 60% $HClO_4$ (11.6 mg, 0.069 mmol) in thf (1 cm^3). The solution was stirred for 10 min and then taken to dryness under vacuum. The solid residue was subjected to t.l.c. On elution with hexane, complex (**3**) (32 mg, 0.05 mmol) was obtained.

Reaction of $[N(PPh_3)_2][Ru_3H(CO)_{11}]$ *with* PhNO *and* $PhNO_2$. To a solution of $[N(PPh_3)_2][Ru_3H(CO)_{11}]$ (34.5 mg, 0.03 mmol) in thf (10 cm^3), PhNO (6.42 mg, 0.06 mmol) or $PhNO_2$ (7.38 mg, 0.06 mmol) was added. The solution was refluxed under argon for 2 min; its colour changed from orange-red to dark brown. Solvent was removed under reduced pressure to yield a brown solid, which was extracted with diethyl ether. The pale yellow ether extract was evaporated to dryness under vacuum to yield a yellow powder (7 mg for PhNO and 2 mg for $PhNO_2$), which was found to be a mixture of $[N(PPh_3)_2][Ru_3H(CO)_9(PhNCO)]$ and $[N(PPh_3)_2]$-$[Ru_3H(CO)_9(PhN)]$ on the basis of a comparison of i.r. and n.m.r. spectra with those of authentic samples.

Reaction of $[N(PPh_3)_2][Ru_3H(CO)_9(PhNCO)]$ *with water and* CO. To a solution of $[N(PPh_3)_2][Ru_3H(CO)_9(PhNCO)]$ (25 mg, 0.020 mmol) in thf (5 cm^3) was added water (50 mg, 2.78 mmol). The solution was stirred at 25 °C for 16 h under a CO atmosphere. It was then concentrated under vacuum and analysed by g.c. to establish the formation of $PhNH_2$. Thin-layer chromatographic work-up with hexane as the eluant yielded a trace of $[Ru_3(CO)_{12}]$ (3 mg, *ca.* 0.004 mmol). Similar results were obtained when the reaction was carried out for 4 h. Reactions of complex (**6**) with water and MeOH were carried out in a similar fashion to establish the formation of $[Ru_3(CO)_{12}]$ and PhNHCHO.

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References

1 G. W. Parshall, in 'Homogeneous Catalysis,' Wiley, New York, 1980, p. 93 and refs. therein; Mitsubishi Chem. Ind. Co., Jap. P. 81 118 054 1982; A. F. M. Iqbal, *Chem. Tech.* (*Leipzig*), 1974, 566; J. F. Kniffon, 'Catalysis in Organic Synthesis,' Academic Press, New York, 1976.

2 F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, 1970, **9**, 342.

3 (*a*) H. Alper and K. E. Hashem, *J. Am. Chem. Soc.*, 1981, **103**, 6514; (*b*) H. Des Abayes and H. Alper, *ibid.*, 1977, **99**, 98; (*c*) H. Alper and N. H. Paik, *Nouv. J. Chim.*, 1978, **2**, 245; (*d*) H. Alper and S. Amaratunga, *Tetrahedron Lett.*, 1980, **21**, 2603.

4 S. Cenini, M. Pizzotti, C. Crotti, F. Porta, and G. La Monica, *J. Chem. Soc., Chem. Commun.*, 1984, 1286.

5 A. Basu, S. Bhaduri, and H. Khwaja, *J. Organomet. Chem.*, 1987, **319**, C28.

6 G. D. Williams, R. R. Whittle, G. L. Geoffroy, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 3936; G. D. Williams, G. L. Geoffroy, G. L. Whittle, and A. L. Rheingold, *ibid.*, 1985, **107**, 729.

7 J. A. Smieja, J. A. Gozum, and W. L. Gladfelter, *Organometallics*, 1987, **6**, 1311; 1986, **5**, 2154.

8 S. H. Han, G. L. Geoffroy, and A. L. Rheingold, *Organometallics*, 1987, **6**, 2380; S. H. Han and G. L. Geoffroy, *ibid.*, 1986, **5**, 2561.

9 S. H. Han, G. L. Geoffroy, and A. L. Rheingold, *Inorg. Chem.*, 1987, **26**, 3426.

10 S. Bhaduri, H. Khwaja, and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1988, 194.

11 S. Bhaduri, H. Khwaja, K. Sharma, and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1989, 515.

12 S. Bhaduri, K. S. Gopalkrishnan, G. M. Sheldrick, W. Clegg, and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1983, 2339.

13 S. Bhaduri, K. S. Gopalkrishnan, W. Clegg, P. G. Jones, G. M. Sheldrick, and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1984, 1765.

14 E. Sappa and L. Milone, *J. Organomet. Chem.*, 1973, **61**, 383.

15 A. Basu, S. Bhaduri, H. Khwaja, and K. R. Sharma, in 'Recent Trends in Inorganic Chemistry,' Indian National Science Academy, New Delhi, 1986; J. A. Smieja and W. L. Gladfelter, *Inorg. Chem.*, 1986, **25**, 2667.

16 (*a*) Y. C. Lin, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1981, **103**, 1216; (*b*) Y. C. Lin, A. Mayr, C. B. Knobler, and H. D. Kaesz, *J. Organomet. Chem.*, 1984, **272**, 207; (*c*) D. Adams, N. M. Golembeski, and J. P. Selegue, *Inorg. Chem.*, 1981, **20**, 1242.

17 A. J. Deeming, Y. Fuchita, K. Hardcastle, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1986, 2259.

18 P. M. Lausarot, G. A. Vaglio, M. Valle, A. Tiripicchio, and M. T. Camellini, *J. Chem. Soc., Chem. Commun.*, 1983, 1391.

19 W. Bernhardt, C. V. Schnering, and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 279.

20 K. Burgess, B. F. G. Johnson, J. Lewis, and P. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 2085; K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *ibid.*, 1981, 2039; C. Choo Yin and A. J. Deeming, *ibid.*, 1974, 1013.

21 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942; F. Piacenti, M. Bianchi, P. Frediani, and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759; C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 838.

22 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.

23 D. F. Shriver and M. A. Drezdzon, 'Manipulation of Air Sensitive Compounds,' Wiley, New York, 1986.

24 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, New York, 1980.

25 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.

26 B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Suss Fink, *J. Chem. Soc., Dalton Trans.*, 1979, 1356.

27 J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, 1974, **15**, 84.

28 'Statistical Methods in Research and Production,' 4th edn., eds. O. L. Davies and P. L. Goldsmith, Longman Group Ltd., New York, 1980.

29 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

30 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

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