DALTON
FULL PAPER

A family of organoruthenium nitrites: alkyne insertion, linkage isomerization and ring nitration

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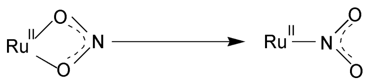
The reaction of [Ru(C_6H_2OH-2-CHNR-3-Me-5)(PPh_3)$_2$(CO)(NO_2)] **1** (R = Et, *p*-MeC_6H_4 or *p*-ClC_6H_4) with an excess of alkyne HC≡CX (X = H, Ph or CH_2OH) in CH_2Cl_2–MeOH medium was accompanied by linkage isomerization of nitrite (*O*,*O*′-bonded ⟶ *N*-bonded) and formation of a six-membered vinyl–phenolato chelate ring to give [Ru(η^2-C_6H_2CXCH-1-*O*-2-CHNHR-3-Me-5)(PPh_3)$_2$(CO)(NO_2)] **4**. The active substrate is the solvate **1**·MeOH, and the 2 + 2 addition of the bulky ≡CX (X = Ph or CH_2OH) group proceeds regiospecifically to the carbon end of the Ru–C bond. Compound **4** has also been obtained metathetically by treating **3** (the chloro analogue of **4**) with $NaNO_2$ in neutral media. However in acid media ring nitration of **3** (R = Et, X = Ph) occurs furnishing [Ru(η^2-C_6HCPhCH-1-*O*-2-CHNHEt-3-NO_2-4-Me-5)(PPh_3)$_2$(CO)Cl] **7** which can metathetically be converted into the corresponding *N*-bonded NO_2 analogue, **8**. The iminium proton is hydrogen bonded to the phenolato oxygen in **4**, **7** and **8** and also weakly to a nitro oxygen in **4** and **8** (IR and ^{1}H NMR data). All the species display a quasireversible cyclic voltammetric Ru^{III}–Ru^{II} couple, the $E_{1/2}$ of which shifts to higher potential by ≈200 mV upon replacing chloride by nitrite (**3** ⟶ **4**; **7** ⟶ **8**) as well as upon aromatic nitration (**3** ⟶ **7**). The crystal structures of the solvate **4b**·C_6H_6 in which R = *p*-MeC_6H_4 and X = H, **4h** in which R = *p*-ClC_6H_4 and X = CH_2OH and **7** have been determined. The σ-vinyl–phenolato chelate ring is approximately planar. The Ru–N bond in the planar $RuNO_2$ fragment of **4b**·C_6H_6 and **4h** is lengthened by ≈0.1 Å due to the *trans* influence of the vinyl group. The Ru–C(vinyl) bond in **7** is significantly shortened due to electron withdrawal by the nitro group, thus promoting Ru–ligand back bonding. The distances of the iminium nitrogen from phenolic oxygen and a nitrito oxygen (in **4b**·C_6H_6 and **4h**) lie in the ranges 2.55–2.67 and 2.90–2.98 Å respectively.

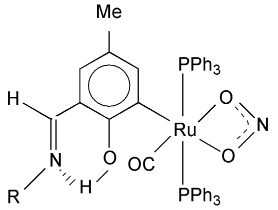
Introduction

Linkage isomerization[1] of ambidentate ligands is of inherent interest in inorganic chemistry, the first reported example being the nitrite ligand.[2] In the present work we describe an unusual instance of such isomerization promoted by insertion of an alkyne into the organoruthenium nitrite **1** incorporating the rare *O*,*O*′-bonded-NO_2 chelation mode. Species of type **1** are formed[3] upon treating the chloride[4–6] **2** with sodium nitrite. It has also been shown that **2** undergoes facile alkyne insertion, the four-membered metallacycle expanding to the six-membered system **3**.[7,8] Instances of alkyne insertion into the Ru–C bond are otherwise relatively sparse.[9–13]

This has prompted us to explore the possible insertion of alkynes into compound **1** where the Ru–C(aryl) bond is unsupported by chelation and to examine the consequence thereof on binding and geometry. Such insertion has indeed been realized, the process being accompanied by linkage isomerization of the coordinated nitrite as in eqn. (1). The nature of the reaction as well as the structures and properties of the new family of *N*-bonded NO_2 organometallics so isolated are scrutinized. We also report an unusual case of nitration of a metallated ring revealed in the course of a search for an alternative route to the *N*-bonded species.



(1)



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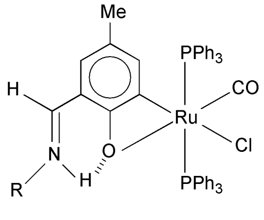

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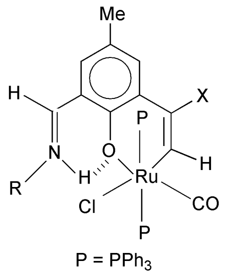

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Results and discussion

Reaction of compound 1 with alkynes: synthesis of Ru(η^2-L)(PPh_3)$_2$(CO)(NO_2) 4

Three type **1** substrates have been employed: R = Et, *p*-MeC_6H_4 or *p*-ClC_6H_4. Upon treating **1** with an excess of alkyne in boiling 2 : 1 CH_2Cl_2–MeOH organometallics of type **4** are afforded in excellent yield, eqn. (2). Eight products (**4a**–**4h**)

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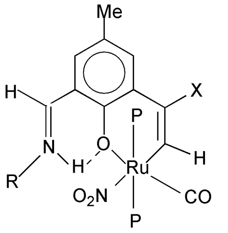
$$\mathbf{1} + \mathrm{HC{\equiv}CX} \longrightarrow \mathbf{4} \qquad (2)$$

$$[\mathrm{X = H, Ph\ or\ CH_2OH}]$$

differing in the R and X substituents of the L ligand (L^1–L^8) have been isolated and characterized. To our knowledge reaction (2) represents the first example of the insertion of propargyl alcohol (X = CH_2OH) into a Ru–C bond.



P = PPh_3

$Ru(\eta^2\text{-}L)(PPh_3)_2(CO)(NO_2)$

	R	X	L
4a	Et	H	L^1
4b	*p*-MeC_6H_4	H	L^2
4c	*p*-ClC_6H_4	H	L^3
4d	Et	Ph	L^4
4e	*p*-MeC_6H_4	Ph	L^5
4f	*p*-ClC_6H_4	Ph	L^6
4g	*p*-MeC_6H_4	CH_2OH	L^7
4h	*p*-ClC_6H_4	CH_2OH	L^8

Reaction (2) is accompanied by several bonding reorganizations as shown by crystallographic and spectroscopic data reported later. Prominent among these are the *O,O′*-bonded $NO_2 \longrightarrow$ *N*-bonded NO_2 isomerization and establishment of six-membered vinyl–phenolato chelation. More subtle changes concern the Schiff base ligand. In **1** the pendant *phenolic* function is hydrogen bonded with the *imine* function. In **4** it is the anionic phenolato function that is coordinated and the hydrogen bonding is now of the *iminium–phenolato* type which also characterizes species of type **2**.[4–6] Owing to steric reasons, the transformation **2** ⟶ **1** is accompanied by rotation of the Schiff base ligand by 180° around the Ru–C bond such that the CO ligand is placed *cis* to the uncoordinated phenolic function.[3] In the reaction **1** ⟶ **4** the phenolic function is utilized for coordination generating the stable six-membered vinyl–phenolato chelate ring. This requires that the original (as in **2**) rotameric conformation (CO *trans* to phenol) be reestablished.

Methanol adduct in solution

Reaction (2) fails to occur in pure dichloromethane and the presence of methanol is essential. Indeed spectrophotometric examination (Fig. 1) in CH_2Cl_2–MeOH mixtures with variable MeOH concentration has revealed the presence of the equilibrium (3). The case of **1** (R = *p*-MeC_6H_4) has been studied in

$$\mathbf{1} + \mathrm{MeOH} \overset{K}{\rightleftharpoons} \mathbf{1}\cdot\mathrm{MeOH} \qquad (3)$$

detail. The band at 510 nm is characteristic of the solvate and the spectra are characterized by an isosbestic point at 361 nm (Fig. 1). The equilibrium constant K at 298 K was found to be $3.81 \times 10^{-2}\ M^{-1}$.

The lack of insertion in pure dichloromethane strongly suggests that it is **1**·MeOH rather than **1** that is the active substrate. We have not succeeded in isolating **1**·MeOH; evaporation of solutions of **1** containing MeOH invariably afforded pure **1** as the only solid product. It is likely that in **1**·MeOH the solvent binds to the metal making nitrite monodentate (presumably *N*-bonded[14]) as stylized in **5**.

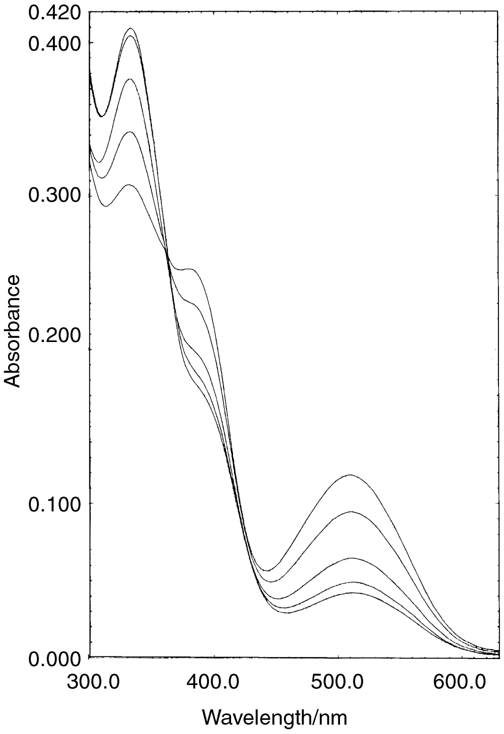
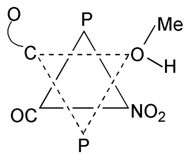
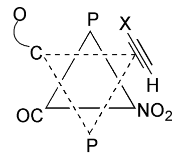


Fig. 1 Spectra of compound **1** (R = *p*-MeC_6H_4, 3.27×10^{-5} M) in CH_2Cl_2–MeOH mixtures corresponding to MeOH concentrations of 3.702, 4.936, 7.404, 12.340 and 17.276 M. The absorbance at 510 nm increases with increasing MeOH concentration.



P = PPh_3

5

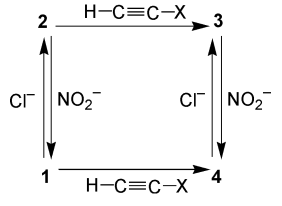


P = PPh_3

6

Regiospecificity and anion metathesis

The alkyne is believed to π-anchor to the metal as in **6** *via* displacement of MeOH from **5**. The subsequent 2 + 2 alkyne addition to the Ru–C bond is subject to steric control by NO_2 and PPh_3 ligands.[7] The bulky ≡CX (X = Ph or CH_2OH) end of the alkyne is thus expected to add regiospecifically to the carbon end of the Ru–C bond. This indeed happens as has been proven directly in the case of propargyl alcohol by structure determination of compound **4h** and indirectly for phenylacetylene *via* metathetical interconversion between **4** (X = Ph) and structurally characterized **3** (X = Ph).[7,8] Such interconversions are readily achieved in dichloromethane–acetone–water media in the presence of an excess of the entering anion. The interrelationship of the species **1**–**4** in terms of insertion and metathesis is set out in Scheme 1.



Scheme 1

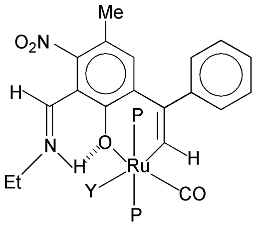
Table 1 Electronic absorption and cyclic voltammetric reduction potential data

Compound (R = Et, X = Ph)	UV-vis data[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Reduction potential[b] $E_{1/2}$/V (ΔE_p/mV)
3	520 (3760)	0.31 (170)
4d	510 (3290)	0.47 (100)
7	555 (3810)	0.52 (110)
8	534 (3816)	0.73 (100)

[a] Solvent is dicholoromethane. [b] Conditions: solvent, dichloromethane; supporting electrolyte, NEt_4ClO_4 (0.1 M); working electrode, platinum; reference electrode, SCE; scan rate 50 mV s^{-1} $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$.

Ring nitration

The metathetical **3** ⟶ **4** conversion occurs in neutral media. In acidic media an entirely different reaction *viz.* aromatic nitration takes place. Thus compound **3** (R = Et; X = Ph) reacts smoothly at room temperature with $NaNO_2$ in dichloromethane solution acidified with acetic acid affording **7** with retention of chloride ligand in nearly quantitative yield. It could be readily converted into **8** by the usual metathetical procedure of Scheme 1 in neutral media. Type **3** compounds other than those noted above also appeared to undergo nuclear nitration by acidified nitrite but we have not succeeded in isolating pure products. Ring nitration of type **2** species could not be achieved at all due to decomposition.



P = PPh3

Ru(η^2-NO_2L^4)(PPh_3)$_2$(CO)(Y)

7 Y = Cl
8 Y = NO_2

Instances of nitration of metallated aryl compounds with retention of the metal–carbon bond are relatively sparse because of reagent promoted decomposition. In a few cases copper(II) nitrate in acetic anhydride has successfully been used.[15,16] The utilization of $NaNO_2$ in acidic dichloromethane for nuclear nitration of organometallics appears to be unprecedented. It has, however, been documented that $NaNO_2$ can nitrate aromatic compounds in acidic media, the reaction proceeding by a free radical pathway in the case of phenols[17,18] and by an electrophilic pathway in the case of simple aromatics.[19] The active reagents are NO_2 and NO_2^+ respectively. Since radical formation is unlikely in our system, the reaction **3** ⟶ **7** probably proceeds by the electrophilic route. Metallation is expected to activate the aromatic ring towards electrophilic substitution. Nitration of **3** occurs selectively in the position *para* to the metallated carbon, the *ortho* position (C3) being hindered by Me and Ph substituents.

Characterization: spectra and reduction potential

Characterization data are collected in the Experimental section. Compounds of type **4**, **7** and **8** display a moderately intense absorption band in the region 500–600 nm. Selected data for a group of compounds with R = Et and X = Ph are listed in Table 1. Two significant energy trends are: a red-shift of the band maximum upon nuclear nitration and a blue-shift upon replacement of chloride by *N*-bonded NO_2. EHMO computations have revealed[8] that this band corresponds approximately to a t_2(Ru) ⟶ π* (metallated ring and aldimine) transition. The observed shifts of the band energy are consistent with this assignment. Nuclear nitration depresses the π* orbital and the *N*-bonded NO_2 ligand (as compared to the chloride ligand) stabilizes[14] the t_2 shell.

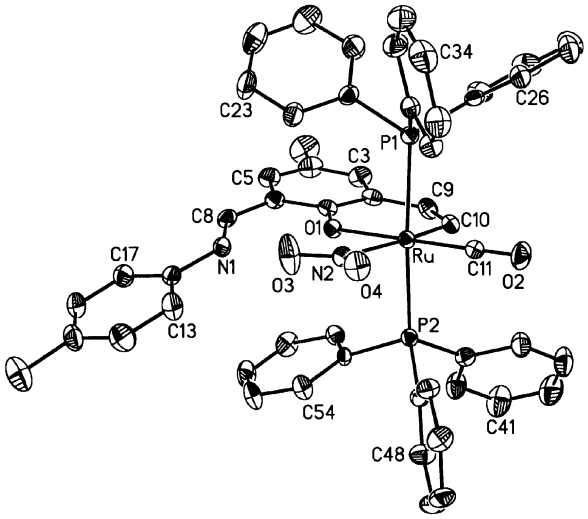


Fig. 2 ORTEP plot (30% probability ellipsoids, as in all Figures) and atom-labeling scheme for compound **4b**·C_6H_6 (excluding C_6H_6).

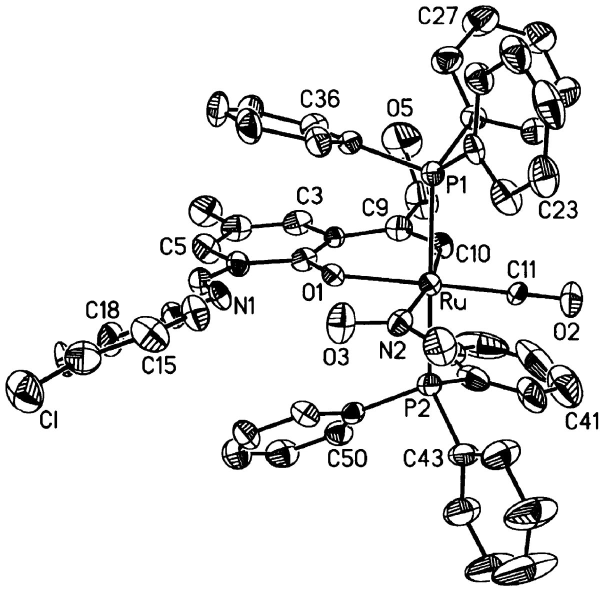


Fig. 3 ORTEP plot for compound **4h**.

In dichloromethane solution the compounds exhibit a quasireversible cyclic voltammetric Ru^{III}–Ru^{II} couple (Table 1). The $E_{1/2}$ of **4** is higher than that of **3**[7] by ≈200 mV consistent with the above-noted stabilization of the redox-active t_2 shell by *N*-bonded NO_2 coordination. Similarly between **7** and **8** there is a shift of ≈200 mV. In going from **3** to **7** nuclear nitration causes a shift of ≈200 mV towards higher potential due to electron withdrawal by the nitro substituent.

Structure

The crystal structures of compounds **4b**·C_6H_6, **4h** and **7** have been determined, authenticating regiospecific alkyne insertion, nitrite isomerization and ring nitration. Molecular views are shown in Figs. 2–4 and selected bond parameters are listed in Tables 2 and 3.

A few general geometrical features will be noted first. In the distorted octahedral coordination sphere the Ru, O1, C10

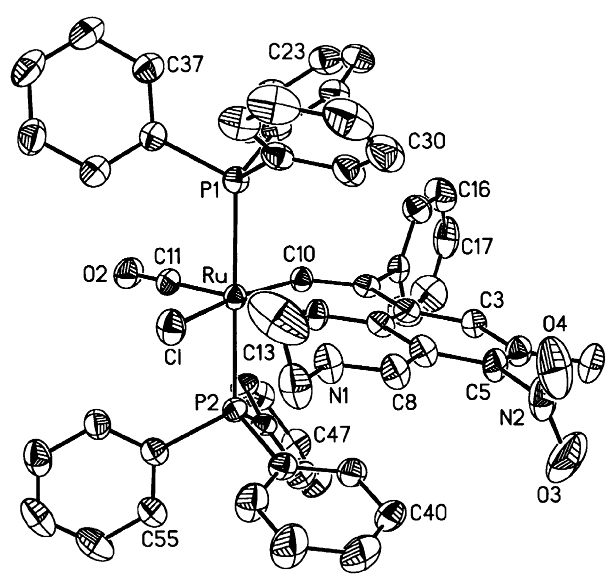


Fig. 4 ORTEP plot for compound **7**.

Table 2 Selected bond distances (Å) and angles (°) for complexes **4b**·C_6H_6 and **4h**

	4b·C_6H_6	**4h**
Ru–P1	2.410(2)	2.387(3)
Ru–P2	2.383(2)	2.395(3)
Ru–C10	2.050(3)	2.041(9)
Ru–O1	2.106(3)	2.077(6)
Ru–C11	1.808(5)	1.825(9)
Ru–N2	2.217(4)	2.176(8)
O1–C1	1.302(5)	1.324(10)
O2–C11	1.157(5)	1.120(11)
N1–C8	1.304(6)	1.345(12)
C9–C10	1.334(1)	1.351(14)
O1 · · · N1	2.668(10)	2.673(10)
N1 · · · O3	2.981(6)	2.897(11)
N2–Ru–P1	92.01(11)	92.3(2)
N2–Ru–C10	170.43(14)	170.8(3)
P1–Ru–C11	89.5(2)	91.6(3)
N2–Ru–O1	83.21(14)	84.4(3)
P1–Ru–C10	88.81(11)	85.0(3)
P1–Ru–P2	175.11(4)	172.88(9)
N2–Ru–C11	97.3(2)	95.7(4)
C10–Ru–C11	92.2(2)	93.2(4)
P1–Ru–O1	90.67(10)	89.3(2)
O1–Ru–C10	87.25(13)	86.8(3)
O1–Ru–C11	179.4(2)	179.1(3)
Ru–C11–O2	177.1(4)	177.3(10)

Table 3 Selected bond distances (Å) and angles (°) for complex **7**

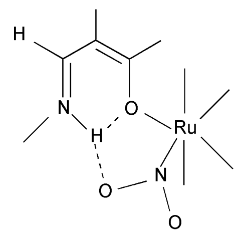
Ru–P1	2.392(2)	Cl–Ru–P1	90.16(6)
Ru–P2	2.382(2)	Cl–Ru–C10	165.2(2)
Ru–C10	2.008(5)	P1–Ru–C11	90.0(2)
Ru–O1	2.066(4)	Cl–Ru–O1	79.68(11)
Ru–C11	1.794(6)	P1–Ru–C10	90.0(2)
Ru–Cl	2.512(2)	P1–Ru–P2	179.54(5)
O1–C1	1.293(7)	Cl–Ru–C11	101.1(2)
O2–C11	1.161(6)	C10–Ru–C11	93.7(2)
N1–C8	1.283(7)	P1–Ru–O1	89.58(11)
C9–C10	1.371(7)	O1–Ru–C10	85.5(2)
O1 · · · N1	2.547(10)	O1–Ru–C11	179.1(2)
		Ru–C11–O2	177.5(5)

atoms together with the carbonyl (C11, O2) and nitrite (N2, O3, O4) ligands define an excellent equatorial plane with mean deviation (md) of 0.01 Å in **4b**·C_6H_6, and 0.03 Å in **4h**. In **7** where Cl replaces NO_2 the planarity is nearly perfect. The six-membered (σ-vinyl) phenolato chelate ring is only approximately planar (md: **4b**·C_6H_6, 0.06; **4h**, 0.04; **7**, 0.08 Å) due to the presence of a fold (**4b**·C_6H_6, 9.2; **4h**, 4.9 **7**, 8.3°) along the C10 · · · O1 line. The plane of the NO_2 group in **7** makes a dihedral angle of 61.0° with the aromatic ring.

The $RuNO_2$ fragment is highly planar (md < 0.01 Å) in both compounds **4b**·C_6H_6 and **4h**. The Ru–N2 length is ≈0.1 Å longer than those normally observed (2.06–2.09 Å)[20–23] in complexes incorporating the Ru–NO_2 moiety due to the *trans* influence of the σ-vinyl group which also lengthens the Ru–Cl bond in **7** as it also does in type **3** species.[7] The Ru–C10 length in **7,** 2.008(5) Å, is significantly shorter than those (2.03–2.05 Å) in **4b**·C_6H_6, **4h** and type **3** species[7] consistent with electron withdrawal by the nitro group and consequent augmented Ru–L[1] backbonding.

Hydrogen bonding

The O1, C1, C6, C8 and N1 atoms define planes with md of 0.04, 0.02 and 0.01 Å respectively in compounds **4b**·C_6H_6, **4h** and **7**. The observed N1 · · · O1 lengths (2.55–2.67 Å) are consistent[7,4–6,14] with zwitterionic iminium–phenolato hydrogen bonding of type $=N^+–H \cdots O^-$. Significantly the *N*-bonded NO_2 group in **4b**·C_6H_6 and **4h** makes relatively small dihedral angles (19.8 and 10.3° respectively) with the plane of the O1, C1, C6, C8 and N1 atoms. The N1 · · · O3 lengths are 2.981(6) and 2.897(11) Å respectively in **4b**·C_6H_6 and **4h**. The iminium function is thus involved in weak bifurcated hydrogen bonding with the O3 atom of the *N*-bonded NO_2 group as highlighted in **9**.



9

The iminium proton has been observed directly in ^1H NMR and IR. In ^1H NMR the N^+–H proton of compound **4** (R = aryl) occurs as a doublet (δ 13.3–14.0, $J \approx 12$ Hz) which disappears upon shaking with D_2O. The doublet structure is due to *trans* coupling with the azomethine proton at δ 7.0–7.5. In **4** (R = alkyl), **7** and **8** the doublet structure of N^+–H is obscured by broadening presumably due to coupling with alkyl protons on the *a*-carbon. The N^+–H resonance of **4** is systematically shifted downfield by ≈1 ppm compared to that[7] (δ ≈ 12) of **3** presumably due to the weak hydrogen bonded interaction between *N*-bonded NO_2 and N^+–H as revealed in the structural work (see **9**). Another notable downfield shift is that of the azomethine proton (δ ≈ 8) in **7** and **8** compared to **3** (δ ≈ 7). In **7** and **8** the azomethine proton lies close to the electron withdrawing aromatic nitro group.

In the IR the N^+–H stretch in compounds **4**, **7** and **8** is observed as a broad feature of medium intensity near 3440 cm^{-1} consistent with weak hydrogen bonding. The C=N stretching frequency is relatively high (≈1630 cm^{-1}) due to the protonation of nitrogen.[7,4–6,24–26]

Conclusion

The facile reaction of compound **1** with alkynes in CH_2Cl_2–MeOH media affording **4** is accompanied by linkage isomerization (1) as well as vinyl–phenolato chelation and bifurcated nitrite–iminium–phenolato hydrogen bonding. The methanol adduct **5** is believed to be the active intermediate in the regiospecific reaction.

In neutral media sodium nitrite causes metathesis as in the reactions **3** ⟶ **4** and **7** ⟶ **8**. However in weakly acidic media it promotes nuclear nitration of type **3** $\longrightarrow$ **7** which constitutes the first example of organometallic aromatic nitration by this reagent. The Ru^{III}–Ru^{II} reduction potentials and $t_2 \longrightarrow \pi^*$ MLCT transition energies undergo characteristic shifts associated with nitrite ligation and nuclear nitration.

Experimental

Materials

The starting materials $Ru(PPh_3)_3Cl_2$,[27] **1**,[3] **2**[4–6] and **3**[7] were prepared by reported methods. Phenylacetylene and propargyl alcohol were obtained from Aldrich and locally available acetylene (in cylinder) was used. Sodium nitrite and other chemicals and solvents were of analytical grade used as received. The purification[28] of dichloromethane and methanol were done as before.

Physical measurements

IR (KBr disc), UV-vis (CH_2Cl_2 solution) and ^1H NMR ($CDCl_3$ solvent, standard $SiMe_4$) spectra were recorded on Perkin-Elmer 783, Shimadzu UVPC 1601 (thermostatted cell compartments) and Bruker 300 MHz FT NMR spectrometers respectively. The numbering scheme used for ^1H NMR is the same as in crystallography. Spin–spin structures are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Microanalyses (C,H,N) were done by using a Perkin-Elmer 240C elemental analyzer. All electrochemical measurements were performed under a nitrogen atmosphere using a PAR 370-4 electrochemistry system.[29] The supporting electrolyte was tetraethylammonium perchlorate and potentials are referenced to the saturated calomel electrode (SCE) without junction correction.

Syntheses

The type **4** complexes were synthesized in ≈85% yields by treating **1** with an excess of alkyne in 2 : 1 CH_2Cl_2–MeOH mixture. Details of representative cases are given below.

[Ru(η^2-L^1)(PPh_3)$_2$(CO)(NO_2)] 4a. A warm solution of compound **1** (R = Et) (50 mg, 0.058 mmol) in 2 : 1 dichloromethane–methanol (50 mL) was purged with acetylene gas and then heated to reflux for 14 h in an acetylene atmosphere with the help of a balloon filled with acetylene. The solution turned from yellow to orange. The solvent was then removed under reduced pressure and the desired compound isolated as an orange solid. Yield 42 mg (82%), mp 168 °C (Found: C, 66.21; H, 4.99; N, 3.14. Calc. for $C_{49}H_{44}N_2O_4P_2Ru$: C, 66.28; H, 4.99; N, 3.16%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 504 (2290) and 361 (3930). IR (KBr, cm^{-1}): 1645(ν_{CN}), 1915 (ν_{CO}), 1270 ($\nu_{asym}(NO_2)$), 1250 ($\nu_{sym}(NO_2)$), 830 ($\delta(NO_2)$) and 3425 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.17 (s, 1H, H^3), 6.39 (s, 1H, H^5), 7.08–7.70 (m, 30H, 2PPh_3 and 1H, CH=C(Ru)), 2.00 (s, 3H, CH_3), 6.09 (d, 1H, C=CH(Ru), J_{HH} 12.0), 13.53 (s, 1H, =N^+–H), 7.45 (d, 1H, CH=N^+, J_{HH} 11.1 Hz), 3.33 (q, 2H, NEt) and 0.87 (t, 3H, NEt). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.51 V (ΔE_p = 160 mV).

[Ru(η^2-L^2)(PPh_3)$_2$(CO)(NO_2)] 4b. Using the same procedure as above, violet, compound **4b** was obtained in 80% yield from **1** (R = *p*-MeC_6H_4), mp 173 °C (Found: C, 68.25; H, 4.87; N, 2.91. Calc. for $C_{54}H_{46}N_2O_4P_2Ru$: C, 68.27; H, 4.88; N, 2.95%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 550 (2560) and 380 (5330). IR (KBr, cm^{-1}): 1620 (ν_{CN}), 1900 (ν_{CO}), 1280 ($\nu_{asym}(NO_2)$), 1260 ($\nu_{sym}(NO_2)$), 830 ($\delta(NO_2)$) and 3440 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.22 (s, 1H, H^3), 6.42 (s, 1H, H^5), 7.10–7.58 (m 34H, 2PPh_3, H^{13}, H^{14}, H^{16}, H^{17} and 1H, CH=C(Ru)), 2.01 and 2.34 (2s, 6H, 2CH_3), 6.12 (d, 1H, C=CH(Ru), J_{HH} 11.4), 13.99 (d, 1H, =N^+–H, J_{HH} 15.0) and 7.43 (d, 1H, CH=N^+, J_{HH} 15.0 Hz). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.57 V (ΔE_p = 140 mV).

[Ru(η^2-L^3)(PPh_3)$_2$(CO)(NO_2)] 4c. This violet solid was obtained in 82% yield from compound **1** (R = *p*-ClC_6H_4) using the same procedure as for **4a**, mp 176 °C (Found: C, 65.62; H, 4.39; N, 2.93. Calc. for $C_{53}H_{43}ClN_2O_4P_2Ru$: C, 65.60; H, 4.47; N, 2.89%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 560 (3730) and 410 (7610). IR (KBr, cm^{-1}): 1615 (ν_{CN}), 1910 (ν_{CO}), 1270 ($\nu_{asym}(NO_2)$), 1260 ($\nu_{sym}(NO_2)$), 820 ($\delta(NO_2)$) and 3435 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.23 (s, 1H, H^3), 6.45 (s, 1H, H^5), 7.12–7.59 (m, 34H, 2PPh_3, H^{13}, H^{14}, H^{16}, H^{17} and 1H, CH=C(Ru)), 2.02 (s, 3H, CH_3), 6.14 (d, 1H, C=CH(Ru), J_{HH} 11.4), 13.98 (d, 1H, =N^+–H, J_{HH} 15.0) and 7.41 (d, 1H, CH=N^+, J_{HH} 15.1 Hz). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.58 V (ΔE_p = 160 mV).

[Ru(η^2-L^4)(PPh_3)$_2$(CO)(NO_2)] 4d. To a yellow solution of compound **1** (R = Et) (50 mg, 0.058 mmol) in 2 : 1 (50 mL) dichloromethane–methanol was added phenylacetylene (45 mg, 0.44 mmol). The reaction mixture was heated to reflux for 9 h turning orange. Upon concentrating and cooling an orange crystalline solid separated, which was collected by filtration and washed thoroughly with methanol and dried *in vacuo*. Yield 47 mg (84%), mp 178 °C (Found: C, 68.51; H, 4.93; N, 2.86. Calc. for $C_{55}H_{48}N_2O_4P_2Ru$: C, 68.53; H, 5.02; N, 2.91%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 510 (3290) and 360 (5170). IR (KBr, cm^{-1}): 1640 (ν_{CN}), 1900 (ν_{CO}), 1260 ($\nu_{asym}(NO_2)$), 1240 ($\nu_{sym}(NO_2)$), 830 ($\delta(NO_2)$) and 3400 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.34 (s, 1H, H^3), 6.97 (s, 1H, H^5), 7.08–7.64 (m, 33H, 2PPh_3, H^{20}, H^{21} and H^{22}), 1.89 (s, 3H, CH_3), 6.25 (s, 1H, C=CH(Ru)), 13.28 (s, 1H, =N^+–H), 7.02 (d, 1H, CH=N^+, J_{HH} 11.1 Hz), 5.94 (m, 2H, H^{19} and H^{23}), 3.17 (q, 2H, NEt) and 1.11 (t, 3H, NEt). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.47 V (ΔE_p = 100 mV).

[Ru(η^2-L^5)(PPh_3)$_2$(CO)(NO_2)] 4e. This was prepared using compound **1** (R = *p*-MeC_6H_4) by the same procedure as a violet solid in 86% yield, mp 175 °C (Found: C, 70.26; H, 4.83; N, 2.71. Calc. for $C_{60}H_{50}N_2O_4P_2Ru$: C, 70.23; H, 4.91; N, 2.73%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 560 (3090) and 405 (6910). IR (KBr, cm^{-1}): 1625 (ν_{CN}), 1915 (ν_{CO}), 1300 ($\nu_{asym}(NO_2)$), 1280 ($\nu_{sym}(NO_2)$), 840 ($\delta(NO_2)$) and 3450 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.39 (s, 1H, H^3), 7.02 (s, 1H, H^5), 7.07–7.58 (m, 37H, 2PPh_3, H^{13}, H^{14}, H^{16}, H^{17}, H^{20}, H^{21} and H^{22}), 2.33 and 1.89 (2s, 6H, 2CH_3), 6.29 (s, 1H, C=CH(Ru)), 13.82 (d, 1H, =N^+–H, J_{HH} 15.0), 7.42 (d, 1H, CH=N^+, J_{HH} 15.0 Hz) and 6.03 (m, 2H, H^{19} and H^{23}). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.53 V (ΔE_p = 110 mV).

[Ru(η^2-L^6)(PPh_3)$_2$(CO)(NO_2)] 4f. The procedure was the same as for compound **4d**: violet crystalline solid, yield 87%, mp 180 °C (Found: C, 67.68; H, 4.45; N, 2.72. Calc. for $C_{59}H_{47}ClN_2O_4P_2Ru$: C, 67.72; H, 4.53; N, 2.68%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 568 (3280) and 410 (7120). IR(KBr, cm^{-1}); 1630 (ν_{CN}), 1920 (ν_{CO}), 1310 ($\nu_{asym}(NO_2)$), 1270 ($\nu_{sym}(NO_2)$), 840 ($\delta(NO_2)$) and 3440 (ν_{NH}, hexachlorobutadiene). ^1H NMR ($CDCl_3$, δ): 6.39 (s, 1H, H^3), 7.01 (s, 1H, H^5), 7.09–7.58 (m, 37H, 2PPh_3, H^{13}, H^{14}, H^{16}, H^{17}, H^{20}, H^{21} and H^{22}), 1.89 (s, 3H, CH_3), 6.29 (s, 1H, C=CH(Ru)), 13.84 (d, 1H, =N^+–H, J_{HH} 12.0), 7.34 (d, 1H, CH=N^+, J_{HH} 12.0 Hz) and 6.02 (m, 2H, H^{19} and H^{23}). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.55 V (ΔE_p = 140 mV).

[Ru(η^2-L^7)(PPh_3)$_2$(CO)(NO_2)] 4g. To a yellow solution of compound **1** (R = *p*-MeC_6H_4) (50 mg, 0.054 mmol) in 2 : 1 (50 mL) dichloromethane–methanol was added propargyl alcohol (30 mg, 0.53 mmol). The reaction mixture was heated to reflux for 6 h, turning violet. Upon concentrating and cooling a violet crystalline solid separated which was collected by

Table 4 Crystal data for complexes **4b**·C_6H_6, **4h** and **7**

	4b·C_6H_6	**4h**	**7**
Formula	$C_{60}H_{52}N_2O_4P_2Ru$	$C_{54}H_{45}ClN_2O_5P_2Ru$	$C_{55}H_{47}ClN_2O_4P_2Ru$
M	1028.05	1000.38	998.41
T/K	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$
a/Å	20.97(2)	14.784(4)	32.572(7)
b/Å	15.677(8)	15.106(4)	12.269(3)
c/Å	30.95(3)	21.971(7)	26.013(5)
β/°	95.70(7)	90.06(3)	99.09(3)
U/Å^3	10123(13)	4907(3)	10265(4)
Z	8	4	8
μ(Mo-Kα) cm^{-1}	4.23	4.88	4.65
Total reflections	6986	7617	5396
Independent reflections (R_{int})	6655 (0.0277)	7232 (0.0268)	5210 (0.0244)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0393, 0.0904	0.0724, 0.1889	0.0436, 0.1194
(all data)	0.0672, 0.1381	0.1188, 0.2655	0.0619, 0.1408

filtration and washed thoroughly with methanol and dried *in vacuo*. Yield: 44 mg (83%), mp 171 °C (Found: C, 67.37; H, 4.87; N, 2.84. Calc. for $C_{55}H_{48}N_2O_5P_2Ru$: C, 67.41; H, 4.94; N, 2.86%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 558 (3205) and 408 (6650). IR (KBr, cm^{-1}): 1625 (ν_{CN}), 1920 (ν_{CO}), 1310 ($\nu_{asym}(NO_2)$), 1280 ($\nu_{sym}(NO_2)$), 830 ($\delta(NO_2)$) and 3440 (ν_{NH}, hexachlorobutadiene). ^{1}H NMR ($CDCl_3$, δ): 7.04 (s, 1H, H^3), 6.34 (s, 1H, C=CH(Ru)), 7.07–7.92 (m, 36H, 2PPh$_3$, H^5, H^{14}, H^{15}, H^{17}, H^{18} and HC=N$^+$), 2.07 and 2.31 (2s, 6H, 2CH$_3$), 3.65–3.71 (m, 2H, CH$_2$), 2.41 (s, 1H, OH) and 13.79 (d, 1H, =N$^+$–H, J_{HH} 15.0 Hz). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.56 V (ΔE_p = 120 mV).

[Ru(η^2-L^8)(PPh$_3$)$_2$(CO)(NO$_2$)] 4h. This was prepared using compound **1** (R = p-ClC$_6$H$_4$) by the same procedure as a violet solid in 85% yield, mp 182 °C (Found: C, 64.79; H, 4.52; N, 2.77. Calc. for $C_{54}H_{45}ClN_2O_5P_2Ru$: C, 64.83; H, 4.53; N, 2.80%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 564 (3820) and 408 (6720). IR (KBr, cm^{-1}): 1620 (ν_{CN}), 1925 (ν_{CO}), 1310 ($\nu_{asym}(NO_2)$), 1270 ($\nu_{sym}(NO_2)$), 830 ($\delta(NO_2)$) and 3430 (ν_{NH}, hexachlorobutadiene). ^{1}H NMR ($CDCl_3$, δ): 7.06 (s, 1H, H^3), 6.34 (s, 1H, C=CH(Ru)), 7.14–7.78 (m, 36H, 2PPh$_3$, H^5, H^{14}, H^{15}, H^{17}, H^{18} and HC=N$^+$), 2.08 (s, 3H, CH$_3$), 3.65–3.75 (m, 2H, CH$_2$), 2.41 (s, 1H, OH) and 13.79 (d, 1H, =N$^+$–H, J_{HH} 15.0 Hz). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.57 V (ΔE_p = 160 mV).

[Ru(η^2-NO$_2$L^4)(PPh$_3$)$_2$(CO)Cl] 7. To a stirring pink solution of compound **3** [40 mg (0.042 mmol) (R = Et, X = Ph)] in 50 mL of dichloromethane were added 0.05 mL glacial acetic acid and 25 mg (0.36 mmol) sodium nitrite. The solution turned violet within a few minutes. Stirring was continued for 15 minutes. The solvent was immediately evaporated under reduced pressure. The solid violet mass was collected by filtration and repeatedly washed with water and dried *in vacuo*. Yield 39 mg (94%), mp 171 °C (Found: C, 66.14; H, 4.69; N, 2.78. Calc. for $C_{55}H_{47}ClN_2O_4P_2Ru$: C, 66.16; H, 4.74; N, 2.81%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 555 (3810) and 415 (3690). IR (KBr, cm^{-1}): 1640 (ν_{CN}), 1900 (ν_{CO}), 1480 ($\nu_{asym}(NO_2)$), 1360 ($\nu_{sym}(NO_2)$), 840 ($\delta(NO_2)$) and 3430 (ν_{NH}, hexachlorobutadiene). ^{1}H NMR ($CDCl_3$, δ): 6.98 (s, 1H, H^3), 6.29 (s, 1H, C=CH(Ru)), 7.00–7.70 (m, 33H, 2PPh$_3$, H^{16}, H^{17} and H^{18}), 12.24 (s, 1H, =N$^+$–H), 1.93 (s, 3H, CH$_3$), 8.13 (s, 1H, CH=N$^+$), 5.81 (m, 2H, H^{15} and H^{19}), 3.72 (q, 2H, NEt) and 0.90 (t, 3H, NEt). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.52 V (ΔE_p = 110 mV).

[Ru(η^2-NO$_2$L^4)(PPh$_3$)$_2$(CO)(NO$_2$)] 8. To a vigorously stirred violet solution of compound **7** (40 mg, 0.040 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added dropwise an aqueous solution (10 mL) of NaNO$_2$ (20 mg, 0.289 mmol). Stirring was continued for 5 h and the violet solution turned pink. The solvent was removed under reduced pressure leaving an aqueous suspension of the pink complex. This was filtered off, washed repeatedly with water and dried *in vacuo*. Yield 39 mg (96%), mp 204 °C (Found: C, 65.32; H, 4.52; N, 4.29. Calc. for $C_{55}H_{47}N_3O_6P_2Ru$: C, 65.47; H, 4.69; N, 4.16%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 534 (3816). IR (KBr, cm^{-1}): 1650 (ν_{CN}), 1920 (ν_{CO}), 1480 ($\nu_{asym}(NO_2)$), 1340, 1250 ($\nu_{sym}(NO_2)$), 850, 825 ($\delta(NO_2)$) and 3445 (ν_{NH}, hexachlorobutadiene). ^{1}H NMR ($CDCl_3$, δ); 6.98 (s, 1H, H^3), 6.27 (s, 1H, C=CH(Ru)), 7.16–7.55 (m, 33H, 2PPh$_3$, H^{16}, H^{17} and H^{18}) 13.65 (s, 1H, =N$^+$H), 1.86 (s, 3H, CH$_3$), 7.93 (s, 1H, CH=N$^+$), 5.94 (m, 2H, H^{15} and H^{19}), 3.21 (q, 2H, NEt) and 1.15 (t, 3H, NEt). $E_{1/2}$-(*vs.* SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.73 V (ΔE_p = 100 mV).

Interconversion of compounds 4 and 3 by metathesis

Upon treating the type **3** species with an excess of NaNO$_2$ in dichloromethane–acetone–water (2 : 2 : 1) followed by vigorous stirring for several hours the type **4** nitro complexes were formed in virtually quantitative yield. The reverse reaction was achieved by similarly treating **4** with an excess of Et$_4$NCl. Representative details are as follows.

To a vigorously stirring pink solution of compound **3** (R = Et, X = H) (40 mg, 0.045 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added dropwise an aqueous solution (10 mL) of NaNO$_2$ (20 mg, 0.289 mmol). Stirring was continued for 4 h until the pink colour turned orange. The solvent was removed under reduced pressure leaving an aqueous suspension of the orange complex. This was filtered off, washed repeatedly with water and the crystalline solid of **4a** was dried *in vacuo*. Yield: 40 mg (99%).

To a vigorously stirring orange solution of compound **4** (R = Et, X = H) (40 mg, 0.045 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added dropwise an aqueous solution (10 mL) of tetraethylammonium chloride (60 mg, 0.362 mmol). Stirring was continued for 4 h until the orange solution turned pink. The solvent was removed under reduced pressure leaving an aqueous suspension of the pink complex. This was filtered off, washed repeatedly with water and the crystalline solid **3** (R = Et, X = H) dried *in vacuo.* Yield: 36 mg (91%).

Determination of equilibrium constant

The reaction was studied spectrophotometrically at 298 K in CH$_2$Cl$_2$–MeOH mixture, the MeOH concentration being in the range 3.7–17.3 M. The concentration of compound **1** (R = p-MeC$_6$H$_4$) was kept constant at 3.27×10^{-5} M. The variation of absorbance (A) at 510 nm with the concentration (M) of methanol is as follows: 0.034, 3.702; 0.041, 4.936; 0.057, 7.404; 0.087, 12.340; 0.110, 17.276. The A values are corrected for the small absorption by **1** (R = p-MeC$_6$H$_4$) at 510 nm as revealed from its spectrum in CH_2Cl_2 solution. The intercept of a linear plot of $[MeOH]^{-1}$ *vs.* A^{-1} (A = absorbance at 510 nm) is the equilibrium constant which equals 3.81×10^{-2} M^{-1}.

Crystallography

Single crystals of compound **4b**·C_6H_6 were grown by slow diffusion of hexane into benzene solution and those of **4h** and **7** by slow diffusion of hexane into dichloromethane solutions. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections. Data were collected by the ω-scan technique on a R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Crystals of **4h** were relatively poorly diffracting with broad peaks. Two check reflections measured after every 198 showed no significant intensity reduction. All data were corrected for Lorentz-polarization effects, and an empirical absorption correction[30] was done on the basis of azimuthal scan of six reflections for each crystal.

In each case the metal atom was located from a Patterson map and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically and hydrogen atoms added at calculated positions. Calculations were performed using the SHELXTL V5.03[31] program package. Significant crystal data are listed in Table 4.

CCDC reference numbers 154175–154177.

See http://www.rsc.org/suppdata/dt/b0/b009719p/ for crystallographic data in CIF or other electronic format.

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