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Some ruthenium complexes containing cyanocarbon ligands: syntheses, structures and extent of electronic communication in binuclear systems

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Abstract

The preparation of several ruthenium complexes containing cyanocarbon anions is reported. Deprotonation (KOBu¹) of [Ru(NCCH₂CN)(PPh₃)₂Cp]PF₆ (1) gives Ru{N=C=CH(CN)}(PPh₃)₂Cp (2), which adds a second [Ru(PPh₃)₂Cp]⁺ unit to give [{Ru(PPh₃)₂Cp}₂(μ -NCCHCN)]⁺ (3). Attempted deprotonation of the latter to give the μ -NCCCN complex was unsuccessful. Similar chemistry with tricyanomethanide anion gives Ru{N=C=C(CN)₂}(PPh₃)₂Cp (4) and [{Ru(PPh₃)₂Cp}₂{ μ -NCC(CN)CN}]PF₆ (5), and with pentacyanopropenide, Ru{N=C=C(CN)C(CN)C(CN)₂}(PPh₃)₂Cp (6) and [{Ru(PPh₃)₂Cp}₂{ μ -NCC(CN)C(CN)C(CN)C-(CN)CN}]PF₆ (7). The Ru(dppe)Cp* analogues of 6 and 7 (8 and 9) were also prepared. Thermolysis of 6 (refluxing toluene, 12 h) results in loss of PPh₃ and formation of the binuclear cyclic complex {Ru(PPh₃)Cp[μ -N=C={C(CN)₂}C(CN)=C(CN)₂}(10). The solid-state structures of 2-4 and 8-10 have been determined and the nature of the isomers shown to be present in solutions of the binuclear cations 7 and 9 by NMR studies has been probed using Hartree–Fock and density functional theory. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ruthenium; Cyanocarbon; Redox properties; Conformations; DFT; Electronic interactions

1. Introduction

The cyano group has been used as a ligand to bridge transition metal centres since the early days of coordination chemistry [1–3]. A great deal of contemporary interest is centred around the use of CN ligands in the design and control of molecular shape, the cyanide-isocyanide isomerism and electron-transfer processes [4,5]. Commonly used metal-containing building blocks include the Fe(dppe)Cp and Ru(PPh₃)₂Cp groups, with one of

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the first reports being given by Davies and coworkers [6]. More recent applications linking these groups to manganese or iron phthalocyanine centres [7], binuclear $Ru_2(\mu-LL)_4$ [LL = MeCO₂, 2-anilinopyridinate, 2-(2-fluoroanilino)pyridinate] centres [8], metal hexafluoro-acetylacetonates [8] and hexanuclear Cu_6 aggregates [9] have been reported. Cyanometallates [10] and carbonyl-cyanometallates [11] have also been used as building blocks for the assembly of a range of unusual manganese derivatives. The ready coordination of organic nitrile groups to metal centres has also resulted in the preparation of many complexes with these ligands bridging two or more metal centres. Examples include various

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dinitriles [12,13], while cyano-carbon and -nitrogen anions have proved to be versatile constituents of electroand magnetically active materials [14]. The structure and electrochemical properties of the anionic complex [W{NCC(CN)C(CN)C(CN)₂}(CO)₅]⁻ have been described [15] and more recently, metal-metal interactions through the CH₂CN bridge in [M(NCCH₂-Fc)(L)₂Cp]PF₆ (M = Fe, Ru; L = PPh₃, dppe/2) have been claimed [16]. Vahrenkamp's perspective [2] allows access to many relevant reviews and papers.

Some earlier studies were directed towards the synthesis of complexes containing cyanocarbons, i.e., organic compounds containing only cyano groups as substituents [17]. On an earlier occasion, we chose to examine the chemistry of cyanocarbon anions and have described several examples of these complexes [18]. Our work with all-carbon bridging ligands, such as the C₄ ligand found in $\{Ru(PPh_3)_2Cp\}_2(\mu-C \equiv CC \equiv C)$ [19,20] and cyanoalkynes such as [C=CCN] and PhC=CCN [21] caused us to reconsider the cyanocarbon complexes as possible precursors of multi-nuclear derivatives which might exhibit electronic communication between the metal centres. This paper describes some studies of complexes derived from cyanocarbon ligands of general form NC-X-CN, including malononitrile $(X = CH_2)$ and its anion $(X = CH^{-})$, and the tricyanomethanide $[X = C(CN)^{-}]$ and pentacyanopropenide $[X = C_3(CN)_3]$ anions, containing $Ru(PR_3)_2Cp'$ $[PR_3 = PPh_3,$ Cp' = Cp; $(PR_3)_2 = dppe; Cp' = Cp^*]$ groups. Comparisons are also drawn with analogous complexes derived from dicyanamide ($X = N^{-}$).

2. Results

On an earlier occasion we described the preparation of $[Ru(NCCH_2CN)(PPh_3)_2Cp]PF_6$ (1) from RuCl-(PPh_3)_2Cp, malononitrile and NH_4PF_6 in methanol [18]. Treatment of 1 with KOBu' in thf gave the neutral complex Ru(NCCHCN)(PPh_3)_2Cp (2) as a bright yellow solid in nearly quantitative yield. Combination of equimolar amounts of 2 with $[Ru(NCMe)(PPh_3)_2Cp]PF_6$ in refluxing thf, followed by precipitation with hexane, afforded binuclear $[{Ru(PPh_3)_2Cp}_2(\mu-NCCHCN)]PF_6$ (3) in 91% yield (Scheme 1).

These compounds were readily characterised by elemental analyses and from their spectroscopic data. For example, the IR spectra contained v(CN) bands between 2100 and 2250 cm^{-1} . The cationic complex 1 gave rise to v(CN) bands at 2269 and 2259 cm⁻¹ which may be compared with that in malononitrile (2305 cm^{-1}) and indicates a limited mixing of the metal and cyanocarbon π -type MOs. The predominant interaction is ligand \rightarrow metal σ -donation through the nitrogen lone pair. The large shift to lower wavenumber which accompanies deprotonation to 2 [v(CN) 2185, 2135 cm⁻¹] suggests a significant degree of mixing between the CN portion of the ligand with the orbital of the same symmetry from the sp^2 -hybridisied C(1) and an increase in the effective conjugation length. Coordination of a second metal fragment in 3 has a negligible effect on the v(CN) frequencies (now 2172 cm⁻¹) indicating limited π -donor/acceptor character is associated with the cyanocarbon anion.



Scheme 1.



Chart 1. NMR data for ligands.

The ¹H NMR spectra contained the expected resonances for Cp and Ph protons. The CH₂ group in 1 gave a broad singlet at δ 3.96, while sharp singlets at δ 2.35 or 4.46 are assigned to the CH protons in 2 and 3, respectively. In the ${}^{13}C$ NMR spectrum of 2, a low intensity CN resonance was present at δ 143.39, while the CH resonances are at δ 4.48 (2) and 9.42 (3). No resonance assignable to the free CN group could be found. These values may be compared with those for $CH_2(CN)_2$ itself $[\delta 8.62 (CH_2), 109.21 (CN)]$ (Chart 1). The electrospray (ES) mass spectrum of 1 contained M^+ at m/z 757, together with fragment ions $[Ru(PPh_3)_nCp]^+$ (*n* = 1, 2) at m/z 429 and 691, respectively. The spectrum of a solution of 2 containing NaOMe contained the ions $[2M + Na]^+$ and $[M + Na]^+$ at m/z 1535 and 779, respectively, together with $[Ru(PPh_3)Cp]^+$ at m/z 429. Complex 3 showed M^+ and loss of up to three PPh₃ ligands.

The compound $Ru{NCC(CN)_2}(PPh_3)_2Cp$ (4) has also been described before and its structure reported [18,22,23]. On this occasion, we give an improved preparation, details of the ¹³C NMR and ES mass spectra which were not previously available, and the X-ray structure of a second, solvated, polymorph. In the IR spectrum, only a single v(CN) band is found at 2172 cm^{-1} , which is virtually unchanged from that in $K[C(CN)_3]$ at 2178 cm⁻¹. Resonances of interest in the 13 C NMR spectrum are at δ 11.29 (central C) and 118.74 (CN) (cf. δ 5.18 and 120.71, respectively, in $K[C(CN)_3]$), both being consistent with the shielding of the central carbon which results from the relatively high electron density on this centre. The Ru–NC resonance is found significantly downfield at δ 133.37. Of interest in the mass spectrum is the presence of binuclear cations at m/z 1472, 1209 and 948, corresponding to $[{Ru(PPh_3)_2Cp}_2C(CN)_3]^+ (\equiv M^+), [M - PPh_3]^+ and$ $[M - 2PPh_3]^+$, respectively.

The binuclear cation was obtained directly in excellent yield as its PF_6^- salt (5) from 4 and a single equivalent amounts of RuCl(PPh₃)₂Cp and NH₄PF₆, or directly from the reaction between RuCl(PPh₃)₂Cp with half an equivalent of K[C(CN)₃] in the presence of NH₄PF₆. Again, characterisation was straight-forward and the spectral properties are unexceptional, the central carbon being found at δ 15.89 (see Section 7). The v(CN) bands from free and coordinated CN moieties could be resolved in this case, being found at 2204 and 2189 cm⁻¹, respectively. During the course of this work, related studies of iron and ruthenium complexes containing dicyanamido and tricyanomethanide groups were described, including **4** and **5** [23]. All attempts using a variety of conditions to add a third Ru(PPh₃)₂Cp group to **5** were unsuccessful, probably for steric reasons.

The bright orange pentacyanopropenide derivative $Ru\{NCC(CN)C(CN)=C(CN)_2\}(PPh_3)_2Cp$ (6; Scheme 1) was obtained from equivalent amounts of RuCl $(PPh_3)_2Cp$ and $[NMe_4][C_3(CN)_5]$ via a minor modification of the method previously described [18]. Use of two equivalents of RuCl(PPh₃)₂Cp with NH₄PF₆ as an additional halide abstracting reagent afforded dark purple [{Ru(PPh₃)₂Cp}₂{ μ -C₃(CN)₅}]PF₆ (7), characterised by elemental analysis and from its ES mass spectrum, which contained ions at m/z 1548 [{Ru(PPh₃)₂Cp}₂C₃- $(CN)_{5}^{\dagger}$ ($\equiv M^{\dagger}$), 1286 ($[M - PPh_{3}]^{\dagger}$) and 1024 $([M - 2PPh_3]^+)$. Similar reactions of one or two equivalents of RuCl(dppe)Cp* with $[C_3(CN)_5]^-$ afforded $Ru\{NCC(CN)C(CN)=C(CN)_2\}(dppe)Cp^*(8) \text{ or } [\{Ru (dppe)Cp^*$ ₂{ μ -C₃(CN)₅}]PF₆ (9), respectively. In addition to the molecular ion $(m/z \ 802)$ and a fragment ion formed by loss of the cyanocarbon ligand, the ES mass spectrum of 8 also featured an isotopic envelope arising from the binuclear complex 9. As detailed in Section 7, the IR spectra of these complexes contain between one and four v(CN) bands, in contrast to the free $[C_3(CN)_5]^-$ anion, which has only one at 2199 cm⁻¹.

The NMR spectra of the pentacyanopropenide complexes revealed the presence of two isomers of the mononuclear complexes **6** and **8** and three isomers of the binuclear complexes **7** and **9** (Table 1). For **7**, the five Cp signals can be assigned to one symmetrical (singlet Cp, relative intensity 0.15) and two unsymmetrical isomers (two pairs of Cp resonances, relative intensities 0.12 and 0.73). For **9**, while only four Cp resonances are found (one signal comprises an overlapping pair), the ³¹P NMR spectrum contains five resonances which

Table 1 Partial NMR spectra of complexes 7, 9 and 10

Complex	7			9			10			
Isomer	1	2	3	1	2	3	1	2	3	4
Ratio	0.73	0.15	0.12	0.54	0.30	0.16	0.59	0.27	0.09	0.05
¹ H (Cp)	4.49, 4.55	4.52	4.54, 4.59	1.45	1.41 ^a	1.38 ^a	4.58	4.52, 4.62	4.54, 4.60	4.74, 4.78
^{31}P (PPh ₃)	40.98, 41.23	41.10	39.99 ^a	74.87	74.77, 76.87	76.69, 77.89	11.88	11.43, 12.35	b	b
¹³ C (Ru-NC)	123.25,	126.88	123.87,	122.77	120.57,	119.64,				
, í	126.79		124.29		122.67	121.43				
¹³ C (Cp)	83.84, 83.87	83.94	83.76, 85.91	9.44	9.31, 9.37	9.08 ^a	78.05	77.71, 78.36	78.20, 78.53	79.90, 80.22
$^{13}C(C_2)$	60.18, 60.92	61.09	58.18, 59.90	59.30	59.07, 59.46	56.56, 57.71	57.91	62.04	b	b

^a Overlapping peaks.

^b Not observed.





[Ru]



(bc) [99.5 / 40.6]





(ad) [13.4 / 2.0]

(ae) [-/36.8]

(**bd**) [0 / 13.7]



Chart 2. Conformations of $[Ru]_x$ -C₃(CN)₅, $[Ru] = Ru(PPh_3)_2$ Cp (x=1, 6; x=2, 7). (a) N-bonded; (b) C-bonded. [Hartree–Fock/DFT calculated relative energies (kJ mol⁻¹) are given in brackets for 6 and 9 or 9-H given in brackets (see text).]

can also be assigned to one symmetrical (intensity 0.54) and two unsymmetrical isomers (intensities 0.30, 0.16). These data are collected in Table 1, which also confirms that all nuclei (1 H, 13 C, 31 P) give consistent spectra. There is no detectable resonance from free PPh₃ and there is no coalescence of any of the resonances on cooling the solutions. Careful t.l.c. did not separate these isomers, nor were products with different NMR spectra obtained after fractional crystallisation.

Consideration of possible points of attachment of the metal centres to the cyanocarbon ligand (Chart 2) indicates that there are three possible isomers of **6** or **8**, and six possible isomers of **7** or **9**. It would appear that facile equilibria between the various components are rapidly set up in solution, although no change in isomeric proportions occurs on cooling or warming the solutions (temperature range -50 to +50 °C). However, different isomeric ratios are found in different solvents, e.g., in C₆D₆ (0.87/0.13), in CDCl₃ (0.71/0.29) or in d₆-acetone (0.79/0.21).

It has not been possible to assign any definitive structures to these isomers. Theoretical calculations (see below) suggest that coordination to the central CN group is likely to be hindered by steric constraints so the isomeric forms involving this arrangement are likely to be those present in minor amounts. Two possible isomers of **6** and **8** are those in which the ruthenium fragment is attached either to one of the cyano groups of the $C(CN)_2$ group (as in **a** or **b**) or to the C(CN) group (as in **c**) and found in the mononuclear derivatives (Chart 2) [3b,15,22,23]. In the cases of **7** and **9**, where several isomers can be detected, the situation is less obvious. On steric grounds it is unlikely that two rutheniums would be attached one to each of the CN groups of one $C(CN)_2$ moiety (isomer **ab**). Assuming then that the first Ru group is attached to one $C(CN)_2$ moiety, the second Ru group can be attached either to the central C(CN) group (ac or bc), or to one of the cyano groups of the second C(CN)₂ moiety (ad, ae or bd). In isomer ae, steric hindrance between the ligands precludes this being formed (see below). Conformational isomerism appears to be inconsistent with the temperature independence of the isomer ratio. While the isomer ratio is solventdependent, inter-conversion of the various forms by a dissociative process seems to be excluded by (a) there being no free PPh₃ detected in solution and (b) there being no change upon addition of $[Ru(thf)(PPh_3)_2Cp]^+$ to a solution of 7.

On heating 6 in refluxing toluene, one PPh₃ ligand is displaced from one molecule by a free CN group of the $C_3(CN)_5$ ligand of a second molecule of complex to give the bright red cyclic complex $\{Ru(PPh_3)Cp[\mu N = C = C \{C(CN) = C(CN)_2 \} CN \}_2$ (10; Scheme 2). This complex is not one of the isomeric products discussed above, as evidenced by its unique ¹H NMR spectrum. This complex was characterised by elemental analysis and (limited) spectroscopic studies, the NMR spectra showing the presence of two major isomers (ratio 0.53/ 0.47), with two other isomers also present in minor amounts. The two major isomers may arise by simple rotation of one of the free $C(CN) = C(CN)_2$ groups relative to the other to give either symmetrical or asymmetrical conformations. The NMR spectra contain three signals for the Cp groups, one a singlet and the other



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a pair of equal intensity signals, which can be assigned to the symmetrical and asymmetrical isomers, respectively.

3. Molecular structures

In previous work, we or others have described X-ray determinations of the molecular structures of $Ru\{N=C=C(CN)_2\}(PPh_3)_2Cp$ (4) [22,23], $Ru\{N=$

C=C(CN)C(CN)=C(CN)₂} {P(OMe)₃}(PPh₃)Cp (6a) [18] and the macrocyclic complex {Ru[C{=C-(CN)₂}C{C=C[Ru(PPh₃)₂Cp]}C(CN)₂](PPh₃)Cp}₂ (11) [19], all containing N-bonded cyano groups. In the latter case, the CN groups are bonded as nitriles, while in the first two, the ketenimine structure is adopted by the (formally) anionic ligands. On this occasion, we report the structures of complexes 2–4 and 8–10. Plots of single molecules or cations are given in Figs. 1–3 and selected structural parameters are collected in Tables 2 and 3.



Fig. 1. (a)–(d) Projections of 2 (molecule 1), 3, 4 [molecule 1, with associated (ordered) solvent] and 8 in common orientation down the Ru–Cp centroid line. 50% amplitude displacement parameters are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. (e) Unit cell contents of 2 projected down a. (f) Unit cell contents of 3 projected down a.



(d)





Fig. 1 (continued)



 $L_2 = (PPh_3)_2$ (7), dppe (9)

3.1. $Ru(NCCRCN)(PPh_3)_2Cp [R = H(2), CN(4)]$

These complexes adopt the usual piano-stool configuration, with the cyano ligands being attached via a nitrogen atom. No unusual bond parameters were found. Thus Ru–P [2.319(1)–2.3338(9) Å], Ru–C(Cp) [2.185–2.239(5) Å] and Ru–N [2.047(4), 2.072(5) (2), 2.051(3) Å (4)] are within ranges previously found, while angles at Ru [P(1)–Ru–P(2) 98.05(4), 99.71(5); 101.18(3); P–Ru–N 88.02(9)–92.7(1), Ru–N–C 173.1–176.5(4)°] are close to those expected for a distorted octahedral geometry. The cyanocarbon ligands are planar, with C–C and C–N distances consistent with the structural representations given above.

3.2. $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}NCCHCN)$ (3)

The binuclear formulation for **3** is confirmed by the structural determination, which shows that the cyanocarbon chain is bent at C(1) [C(11)-C(1)-C(12) $121.2(8)^{\circ}]$. Other parameters within this group are normal: N-C 1.163(9), 1.17(1); C-C 1.38, 1.37(1) Å, angles Ru(1)-N-C 173.8°; N-C-C 178.0°.



Fig. 2. Projections of **10**, (a) normal to and (b) through, the central ring 'plane'.

3.3. $Ru\{NCC(CN)C(CN)C(CN)_2\}(dppe)Cp^*(8)$

The anionic cyanocarbon is attached via a nitrogen, leading to the ketenimine configuration with approximate linear Ru–N–C arrangement, as found in the analogous complex described earlier [Ru–N 2.012(2) (8), 2.033(6) Å (8b); Ru–N(11)–C(11) 166.9(2)° (8), 176.3(4)° (8b)] [18]. In this case, the Ru–P [2.3066, 2.3072(6) Å] and Ru–C(Cp*) distances [2.223–2.255(2) Å] are similar to those found in other examples, the chelating phosphine resulting in a smaller P–Ru–P angle [83.65(2)°] and P–Ru–N angles [85.59°, 90.52(6)°],



Fig. 3. Projection of 9 approximately through the Cp* ring planes, showing the disorder associated with the central cyanocarbon ligand.

Table 2			
Selected	bond	parameters	for 2–4

	2 (mols 1, 2)	3 ^a	4 ^b
Bond lengths (Å)			
Ru-P(1)	2.322, 2.327(1)	2.319(2)	2.3338(9)
Ru–P(2)	2.327(1), 2.319(1)	2.327(2)	2.327(1)
Ru–C(cp)	2.206-2.239(5), 2.212-2.225(6)	2.192-2.239(8)	2.185-2.236(5)
(av.)	2.22(1), 2.217(5)	2.22(2)	2.21(2)
Ru–N(11)	2.047(4), 2.072(5)	2.053(6)	2.051(3)
N(11)–C(11)	1.149(6), 1.152(8)	1.163(9)	1.150(5)
C(1)–C(11)	1.383(8), 1.47(1)	1.38(1)	1.389(6)
C(1)–C(12)	1.386(8), 1.27(1)	1.37(1)	1.396(7)
C(12)–N(12)	1.158(8), 1.25(2)	1.17(1)	1.159(8)
Bond angles (°)			
P(1)-Ru-P(2)	98.05(4), 99.71(5)	100.96(6)	101.18(3)
P(1)-Ru-N(11)	90.2(1), 90.0(1)	87.0(2)	89.99(9)
P(2)–Ru–N(11)	92.7(1), 91.9(1)	88.1(2)	88.02(9)
Ru–N(11)–C(11)	173.1(4), 176.5(4)	173.8(5)	174.8(3)
N(11)-C(11)-C(1)	177.6(5), 171.6(8)	178.0(7)	176.6(5)
C(11)-C(1)-C(12)	118.4(5), 124.9(9)	121.2(8)	118.7(4)
C(1)-C(12)-N(12)	179.4(6), 173(1)	176.2(9)	177.6(6)

^a Ru(1) ambience only; Ru(2) is similar but disordered.

^b C(1)–C(13) 1.388(7), C(13)–N(13) 1.144(8) Å; C(11)–C(1)–C(13) 122.1(4)°, C(1)–C(13)–N(13)178.5(6)°.

than those found in 2 and 4 above. The cyanocarbon ligand is planar.

3.4.
$$\{Ru(PPh_3)_2Cp\}_2\{\mu-NC(CN)C(CN)C(CN)CN\}$$
 (9)

Although this structure is imprecise and further discussion of the molecular parameters is thereby precluded, the determination confirms the formulation, being modelled in terms of two conformations with equal occupancies (Fig. 3). As discussed below, these appear to be related to the minimum energy conformations **9bd** and **9bd'** found by theoretical calculations, which are related by a ca 180° rotation about the Ru–N bond (Fig. 4).

3.5. $\{Ru(PPh_3)Cp[\mu-NCC[C(CN)C(CN)_2]CN]\}_2$ (10)

Although formally the cyanocarbon ligand is attached by a ketenimine group to one ruthenium and

Table 3 Selected bond parameters for **8–10**

	8	9 [Ru(1, 2)]	Calc. ^a	10
Bond lengths (Å)				
Ru-P(1)	2.3066, 2.3072(6)	2.306(6); 2.280(6)		2.325(1)
Ru–C(cp)	2.223-2.255(2)	2.22-2.24(3); 2.19-2.24(2)		2.164-2.212(5)
(av.)	2.24(1)	2.23(1); 2.22(2)		2.18(2)
Ru–N(11)	2.012(2)	2.00(2); 2.01(2)	2.16; 2.17	2.042(4)
N(11)-C(11)	1.149(3)	1.06(4); 1.15(4)	1.15; 1.15	1.136(7)
C(1)–C(11)	1.420(4)			1.419(7)
C(1)-C(12)	1.426(5)			1.419(5)
C(1)–C(2)	1.386(4)	1.55(5); 1.40(7)	1.44; 1.44	1.37(2)
C(2)–C(3)	1.345(5)	1.31(11); 1.51(13)	1.41; 1.41	1.38(2)
C(2)–C(21)	1.552(5)	1.39(4); 1.50(9)	1.44; 1.44	1.46(1)
C(3)–C(31)	1.458(5)	1.37(13)	1.47; 1.47	1.46(2)
C(3)–C(32)	1.382(5)			1.42(2)
C(12)–N(12)	1.133(5)			1.146(5)
C(21)–N(21)	1.125(5)			1.14(3)
C(31)–N(31)	1.111(5)			1.09(2)
C(32)–N(32)	1.121(4)			1.12(2)
Bond angles (°)				
P(1)-Ru-P(2)	83.65(2)	83.4(2); 84.3(2)		
P(1)-Ru-N(11)	85.59(6)	92.4(6); 87.7(6)		88.5(1)
P(2)-Ru-N(11)	90.52(6)	89.4(6); 86.4(6)		
Ru–N(11)–C(11)	166.9(2)	167(2); 159(3)	175.9; 178.0	169.2(4)
N(11)-C(11)-C(1)	170.8(3)	168(3)	175.7; 175.7	172.9(4)
C(11)-C(1)-C(2)	126.0(3)			113.4(6)
C(11)-C(1)-C(12)	116.6(2)			115.3(4)
C(1)-C(2)-C(3)	129.2(3)	101(6); 121(6)	121.2; 121.2	124.3(8)
C(1)-C(2)-C(21)	116.6(2)		113.6; 113.7	120(1)
C(1)-C(12)-N(12)	175.5(3)			174.5(6)
C(2)-C(3)-C(31)	118.3(3)		115.4; 115.4	119.9(9)
C(2)–C(3)–C(32)	122.5(3)			123(1)
C(2)-C(21)-N(21)	176.0(4)			175(2)
C(3)-C(31)-N(31)	174.9(4)			175(2)
C(3)-C(32)-N(32)	170.9(4)			176(2)

For 9: Ru–P(2) 2.308(6); 2.279(7) Å.

For 10: Values for the ligand are for the major component; values for C(N)(3, 31, 32), C(N)(4, 41, 42) are tabulated as the second component of C(N)(2, 21, 22), C(N)(1, 11, 12). P(1)-Ru-N(12) 91.1(2), N(11)-Ru-N(12) 84.8(2) Å; Ru-N(12)-C(12) 171.0(3)°.

^a See text.

a nitrile group to the other, the complex is centrosymmetric and therefore both Ru-NC bond distances are equivalent. The cyanocarbon ligand and two Ru atoms are coplanar. The Ru-P [2.325(1) Å] and Ru-N [2.042(4) Å] distances closely resemble those mentioned above, as do the angles at Ru [N-Ru-N 84.8(2)°, N-Ru-P 88.5°, 91.1(2)°], but the Ru-C(Cp) [2.164-2.212(5) A] distances are somewhat shorter, probably as a result of decreased steric hindrance (only one PPh₃ group). An alternative explanation for the change in bond length may be related to the altered electronic environment around the metal centre, which with only one PPh₃ ligand is less electron-rich, resulting in increased electron donation from the Cp ligand and shorter Ru–C(Cp) bond lengths. Apparently, metal \rightarrow ligand back-donation is not important here.

4. Electrochemistry

With a view to assessing the degree to which the metal centres might interact via the various cyanocarbon ligands NC–X–CN, we have briefly examined the electrochemical properties of these complexes, determining their cyclic voltammograms using similar conditions (see Section 7 and Table 4).

The mononuclear cation **1** undergoes a single partially reversible oxidation at $E^0 = +1.38$ V, which is similar to that found for [Ru(NCPh)(PPh₃)₂Cp]⁺ under comparable conditions (+1.30 V [21]). As expected, neutral **2** is oxidised at much lower potentials ($E^0 = +0.51$ V; irreversible), the CV also containing a partially reversible oxidative wave ($E^0 = +1.38$ V) which we ascribe to the oxidation of **1** formed at the electrode



Fig. 4. Projections of the structures of the three lowest-energy conformers (a) **9bd**, (b) **9bd**' and (c) **9ad**, determined at the ab initio Hartree–Fock level of theory. Hydrogen atoms have been omitted for clarity.

Table 4 Some electrochemical data for ruthenium-cyanocarbon complexes

Complex/X	E_1 (V)	E_2 (V)	$\Delta E (mV)$	E_3 (V)
1/CH ₂	1.38 (part rev.)	_		
2/CH ⁻	0.51 (irrev.)			
3/CH ⁻	0.59	1.09	500	_
4/C(CN) ⁻	0.97	_		_
5/C(CN)-	0.95	1.18	230	_
$6/C_3(CN)_3^{-1}$	1.14	_		-1.30
$7/C_3(CN)_3^{-1}$	1.17	1.34	300	-1.15
$8/C_3(CN)_3^{-1}$	0.92	_		-1.33
$9/C_3(CN)_3^{-1}$	0.91	1.13 (irrev.)	220	-1.23
$10/C_3(CN)_3^-$	1.10	1.28 (part rev.)	180	-1.411.25

surface after oxidation of **2**. Introduction of an additional electron-withdrawing CN group in the tricyanomethanide complex **4** raises the oxidation potential to +0.97 V. In comparison with the other ligands in this series, the poorer σ -donor properties of the pentacyanopropenide group are clearly shown by the oxidation

potential of neutral **6** (+1.14 V). Introduction of a more electron-rich metal centre [Ru(dppe)Cp*] lowers the oxidation potential of **8** (+0.92 V) compared with the Ru(PPh₃)₂Cp analogue **6**.

For the binuclear complex 3, we find two fully reversible oxidation waves at $E^0 = +0.59$ and +1.09 V, while 4 gives only one reversible wave at $E^0 = +0.97$ V. Two processes at $E^0 = +0.95$ and +1.18 V were found for 5. Introduction of the extensively delocalised bridging $C_3(CN)_3$ moiety in 7 and 9 also results in two oxidation processes separated by 300 or 220 mV, respectively, reflecting the differing electron richness of the two metal centres. The doubly-bridged system in 10 gives two oxidation potentials, separated by ca 180 mV. Complexes 6–10 also exhibit reduction waves at potentials between -1.23 and -1.41 V, the extended polycyanocarbon ligand allowing electron delocalisation onto the CN groups and thus stabilisation of the anionic species formed by population of the ligand π^* MOs. The similarity of the reduction potentials found for 6 and 8, and for 7 and 9, confirms the limited metal \rightarrow ligand back-donation suggested by the IR v(CN) spectra.

5. Discussion

We have examined the coordinating abilities of the free CN groups in some ruthenium cyanocarbon complexes towards a second Ru(PP)Cp' moiety $[PP = (PPh_3)_2, Cp' = Cp; PP = dppe, Cp' = Cp*]$, finding that binuclear complexes are formed readily in essentially quantitative yield. Indeed, in solution, the ES mass spectra suggest that such species form readily even when a deficiency of ruthenium is present, at least under ES mass spectroscopic conditions. X-ray structure determinations confirm the anticipated *N*-bonding of the cyanocarbon ligand, as found in several earlier examples.¹

As mentioned above, three isomers can be detected by NMR spectroscopy for both 7 and 9 (Table 1). While definitive assignments of these resonances to particular isomers cannot be made, it is informative to consider the particular structures which are possible (Chart 2) and to compare their energies by theoretical calculations. We assume that one ruthenium fragment is attached to a CN group of one of the $C(CN)_2$ moieties, as found in the structure of the mononuclear complex 8. Six isomeric arrangements of the two Ru fragments can then be drawn (Chart 2, ab, ac, ad, ae, bc and bd). The second Ru group can be bonded either to the central C(CN) group or to a CN group of the second C(CN)₂ group. With restricted rotation about the $C(CN)-C(CN)_2$ bond, related structures **ac** and **bc** give a symmetrical structure which may be responsible for the singlet resonance. Isomer **ab** arises by coordination of Ru moieties to both CN groups of a single $C(CN)_2$ group. Although sterically congested, theoretical calculations suggest that it is possible for this to form, unlike isomer ae, for which no sensible structure can be calculated.

Our studies have shown that the isomer ratios are solvent dependent, but are not affected by temperature. Interconversion of various isomers by a dissociative process seems to be excluded by (a) there being no resonance assignable to free PPh₃ present and (b) there being no change in ratio upon addition of $[Ru(thf)-(PPh_3)_2Cp]^+$.

5.1. Hartree–Fock and density functional theory calculations

Conformers 9ab, 9ac, 9ad, 9bc and 9bd (see Chart 2) were first investigated via the ab initio Hartree-Fock (HF) approach. The close proximity of the Ru(dppe)Cp* groups makes isomer 9ae sterically disfavoured and this structure was not considered further. The relative energies calculated for the complexes investigated are given in parentheses in Chart 2. According to the HF results, the energetically most stable structure is 9bd. In this structure the two Cp* groups are oriented in the same direction. The next lowest energy structure is denoted as 9bd', in which the molecular conformation has the relative orientation of one Ru(dppe)Cp* group rotated by $\sim 180^{\circ}$ about the cyanocarbon quasi-plane. The small difference in energies (6.5 kJ mol⁻¹) between **9bd** and **9bd**' suggests that rotation of the Ru(dppe)Cp* group about the adjacent C–N bond axes is relatively unhindered.

The next two lowest energy conformers are **9ad** and **9ac**, lying, respectively, 13.4 and 14.9 kJ mol⁻¹ higher in energy than **9bd**. Conformer **9ab**, which has the two Ru(dppe)Cp* moieties on adjacent CN groups, lies 35.1 kJ mol^{-1} higher in energy, while conformer **9bc** [also having Ru(dppe)Cp* moieties on adjacent CN groups] is calculated to be the least favoured structure, lying 99.5 kJ mol⁻¹ higher than **9bd**.

Conformers of the analogous model complex $\{Ru(dHpe)Cp\}_2C_3(CN)_5$ (9-H; $dHpe = PH_2CH_2CH_2-PH_2$; see Fig. 4) were also computed via density functional theory (DFT) for comparison. Their relative

¹ It is rare for transition metal derivatives of the cyanocarbons to be other than N-bonded, with the exception of the η^2 -alkene complexes formed by tetracyanoethene [24]. However, the Ru(PPh₃)₂Cp complex derived from (phenylsulfonyl)acetonitrile has recently been shown to exist in the N- and C-bonded forms, the former being the more stable [25]. Interconversion by intra- and inter-molecular mechanisms were demonstrated. The rates of isomerisation of related complexes carrying different tertiary phosphine ligands appear to depend on the cone angle of the phosphine, i.e., to be influenced by steric effects, there being no correlation with the basicity of the phosphine. In the present case, two C-bonded isomers can be formulated (**f** and **g**, Chart 2). We have been able to isolate only one form of the complexes, although solutions of extensively purified material show the same ratio of isomers.

energies are also given in brackets in Chart 2. The fact that structure **9-Hbd** is not the most stable arrangement according to DFT results clearly indicates that steric hindrance, e.g., between ligand phenyl groups, is a major factor in determining the stabilities of the different isomers. Interestingly enough, the energies of the other conformers of **9-H**, namely **ab**, **ac**, **ad** and **bd**, track those obtained at the HF level of theory (see Chart 2).

Different possible conformations of hydrogenated models of mononuclear **6** [Ru{C₃(CN)₅}(PH₃)₂Cp, (**6**-**H**)] were also computed at the DFT level of theory. The results indicate that structure **6-Ha** is energetically preferred over structures **6-Hb** and **6-Hc** by 12.5 and 14.5 kJ mol⁻¹, respectively.

As can be seen from Fig. 4, the conformations found experimentally in the X-ray crystal structure determination for 9 closely resemble those of 9ad and 9bd. The observed disorder confirms the presence of both conformers and provides evidence for the relatively unhindered rotation described above. The calculated structural parameters are compared with the values determined from the X-ray structural study (Table 3) which, however, are of relatively low precision. The cyanocarbon groups in the two conformers 9bd and 9bd' are almost unaltered by the rotation about the Ru(1)-N(1) bond. In addition, the distance between the centroids of the two Cp* groups differs by only 1.84 A. As expected, the calculated bond lengths are somewhat longer than those found in the structure determination.

The conformational study was carried out, in part, to try to cast light on the mixture of conformers which were detected in solution by NMR methods. While no quantitative conclusions can be drawn, it is interesting to find that of the five conformers (Chart 2) which could be calculated, the relative energies appear to correlate quite well with the relative concentrations of each conformer found in solutions of 9. Indeed, conformer 9bd could tentatively be assigned to the symmetrical NMR isomer, whereas 9ac and 9ad could correspond to the two unsymmetrical NMR isomers (see above). We must mention, however, that calculations were performed on isolated molecules without taking into account polar solvent effects which may play a role in favouring one isomer or another. No doubt similar conformational isomers are responsible for the several resonances also found in solutions of the other complexes described above.

The possibility of further deprotonation of **2** to the neutral species, which would contain the conjugated Ru-N=C=C=C=N-Ru sequence, resembling similar complexes containing C_n chains, was explored. However, we have been unable to perform this transformation (using NaOMe, LiMe, KOBu^t or LiH as bases), since the presence of the two nitrogen atoms would undoubtedly make this species considerably more basic

than the related complexes $[{Cp(R_3P)_2M}]=C=C=CHC=C{M(PR_3)_2Cp}]BF_4$ [M = Fe, (PR_3)_2 = dppe; M = Ru, Os, PR_3 = PPh_3], whose syntheses were described by Jia [26]. Attempts to prepare complexes containing the μ -C₅ ligand by treating the cations with [CPh₃]⁺ or with strong bases were unsuccessful.

5.2. Electrochemistry

Single oxidation processes were found in the CVs of the mononuclear complexes 1, 2, 4, 6 and 8, that for 1 being at a much higher potential as expected for a cationic complex. The oxidation potentials are consistent with the differing electron densities at the metal centres in the end-capping $Ru(PPh_3)_2Cp$ and $Ru(dppe)Cp^*$ groups, and with the poorer electron-donor properties of bridging groups with more CN substituents.

Some indication of the degree of interaction between the metal centres through the bridging ligand can be obtained by considering differences between the two 1-electron redox potentials (ΔE^0) found for the binuclear complexes. Previous studies have shown that this is a feature of many complexes containing electron-rich metal centres linked by a C₄ chain [27]. Others have shown that electronic interactions diminish as the carbon chain length increases [28]. Electrochemical measurements on the binuclear complexes 3, 5, 7, 9 and 10 confirmed that there is an electronic interaction between the two ruthenium centres, which is mediated by the cyanocarbon chain. However, the oxidised species could not be isolated after treatment of the complexes with ferrocenium ion or Ag⁺, for example, only intractable brown solids being obtained.

Further consideration of the differences in redox potentials in terms of the bridging group X in the ligands $[NC-X-CN]^-$ shows a decrease in the order X = H (3; 500 mV) > C₃(CN)₅ (300 for 7, 200 for 9) > CN (5; 230) > N (180 [23]). Corresponding values for K_C for 3 and 5 are 2.8×10^8 and 7.7×10^3 , respectively. While the HOMO is likely to be similar to that found in $\{Ru(dppe)Cp^*\}_2(\mu-C_4)$, in that it is derived from mixing of the filled d orbital with the filled ligand set [20a], the substituent on the central carbon exerts an inductive effect to moderate the contribution of the central carbon to the HOMO, in turn moderating the degree of perturbation between the metal centres.

For complexes 1, 2 and 3, no reduction processes were observed within the solvent limits.

In the binuclear derivatives 7 and 9, a fully reversible reduction wave is observed, presumably from a ligandcentred event. As expected, the reduction process is more negative for the Ru(dppe)Cp* complexes as a consequence of the greater inductive electron-donating properties of this fragment, i.e., they are more readily oxidised than the Ru(PPh₃)₂Cp complexes. Complex 10 shows two reduction and two oxidation waves, all fully reversible. The first oxidation potential is found at relatively high potentials for a neutral complex within this series, a consequence of both the presence of a poorly electron-donating pentacyanopropenide ligand and the decrease in the number of phosphine ligands about each metal centre. The observation of two distinct reduction potentials in this complex, but only one in the related binuclear complexes 7 and 9, suggests that these processes are a consequence of a through-space interaction between ligand-centred anions.

It is therefore apparent that the degree of interaction between the metal centres in complexes of general form $[{Ru(PP)Cp'}_2{\mu-X(CN)_2}]^+$ can be tuned by subtle changes in the ligand structure, with electron-withdrawing substituents decreasing both the electron density between the metal centres and the magnitude of the through-bond coupling component.

6. Conclusions

We have prepared several complexes containing Ru(PP)Cp' groups attached to various cyanocarbon fragments. In the case of complexes where two of these fragments are bridged by the cyanocarbon ligand, electrochemical measurements demonstrated that there is a moderate to high degree of electronic interaction between the two metal centres. After the completion of this study, Chen and coworkers [8a] published an independent study of dicyanamide and tricyanomethanide-bridged iron and ruthenium complexes, which contained a structural study of the monohydrate of 4 (which is isomorphous with the CHCl₃-solvate reported here). Where they overlap, there is substantial agreement between our two sets of results. Finally, Hartree-Fock and density functional theory calculations on the conformers of 6and 9, carried out to provide information concerning the various species detected by NMR in solution, predict several conformations close in energy, two of which are found in the crystal structure. This series, taken together with the related dicyanamide complex $\{Ru(PPh_3)_2Cp\}_2$ - $\{\mu$ -N(CN)₂ $\}$ allows for a comparison of the electronic interactions between the metal centres mediated by the ligand series NC-X-CN (X = CH₂, [CH]⁻, [C(CN)]⁻, $[C_3(CN)_3]^-$), which are attenuated by the more electronwithdrawing substituents.

7. Experimental

7.1. General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to ex-

clude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Preparative t.l.c. was carried out on glass plates (20×20 cm) coated with silica gel (Merck 60 GF₂₅₄, 0.5 mm thickness).

7.2. Instrumentation

IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.105 MHz) or Varian Gemini 200 (¹H at 199.8 MHz, ¹³C at 50.29 MHz) spectrometers. Unless otherwise stated, spectra were recorded using solutions in CDCl₃ in 5 mm sample tubes. ES mass spectra: Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [29]. Electrochemistry was carried out with a MacLab 400 instrument. The CVs were determined under standard conditions at room temperature (1.0 mM solutions in CH₂Cl₂ containing 0.1 M [NBu₄]PF₆ as supporting electrolyte). A three-electrode system was used, consisting of a Pt-dot working electrode and Pt counter and pseudo-reference electrodes. Potentials (see Table 4) are given in V vs SCE, the ferrocene-ferrocinium couple being used as internal calibrant for the measured potentials ($E^0 = +0.46$ V vs SCE) [30].

7.3. Reagents

The compounds $K[C(CN)_3]$ [17a], $[NMe_4][C_3(CN)_5]$ [17a], $RuCl(PPh_3)_2Cp$ [31] and $RuCl(dppe)Cp^*$ [20b] were prepared by literature methods.

7.3.1. $[Ru(NCCH_2CN)(PPh_3)_2Cp][PF_6]$ (1)

A suspension of RuCl(PPh₃)₂Cp (400 mg, 0.55 mmol), NH₄PF₆ (200 mg, 1.22 mmol) and malononitrile (80 mg, 1.05 mmol) in degassed MeOH (15 ml) was stirred for 3 h. The resulting bright yellow precipitate was collected on a sintered glass funnel and washed with benzene (20 ml) followed by Et₂O (20 ml) before being dried under vacuum to give [Ru(NCCH₂CN)-(PPh₃)₂Cp][PF₆] (1) (421 mg, 85%). IR (nujol): v(CN) 2259, 2269; v(PF) 839 cm⁻¹. H NMR: δ 7.02–7.40 (m, 30H, Ph), 4.52 (s, 5H Cp), 3.96 (br, 2H, CH₂). ¹³C NMR: δ 128.34-135.53 (m, Ph), 121.06 (s, Ru-NC), 108.65 (s, CN), 83.90 (s, Cp), 10.58 (s, CH₂). ³¹P NMR: δ 41.65 (s, PPh₃), -143.11 (septet, PF₆). ES mass spectrum (positive ion mode, m/z): 757, M⁺; 691, $[Ru(PPh_3)_2Cp]^+$; 429, $[Ru(PPh_3)Cp]^+$. Lit. values [18]: IR (nujol) 2267 cm⁻¹; ¹H NMR (CDCl₃): δ 7.31 (Ph), 4.56 (Cp), 3.96 (CH₂).

7.3.2. $Ru(NCCHCN)(PPh_3)_2Cp(2)$

To a solution of 1 (980 mg, 1.09 mmol) in thf (20 ml) was added KOBu^t (123 mg, 1.09 mmol) and the solution

was stirred at r.t. for 15 min. Solvent was removed under vacuum and a CH₂Cl₂ extract of the solid was filtered into rapidly stirred hexane to give a bright yellow precipitate that was collected on a sintered glass funnel to give Ru(NCCHCN)(PPh₃)₂Cp (**2**) (797 mg, 97%), which was characterised by comparison with the published data. IR (nujol): v(CN) 2185, 2135 cm⁻¹. ¹H NMR (C₆D₆): δ 6.95–7.28(m, 30 H, Ph), 4.00 (s, 5H, Cp), 2.35 (s, 1H, CH). ¹³C NMR: δ 143.39 (s, NC-Ru), 127.30–136.92 (m, Ph), 82.07 (s, Cp), 4.48 (s, CH). ³¹P NMR: δ 42.15 (s, PPh₃). ES mass spectrum (positive ion mode, with NaOMe, *m*/*z*): 1535, [2M + Na]⁺; 779, [M + Na]⁺; 429 [Ru(PPh₃)Cp]⁺. (Lit. values [18]: IR *v*(CN) 2231vw, 2161 (sh), 2137s cm⁻¹; ¹H NMR: δ 4.24s, 7.24m).

7.3.3. $[{Ru(PPh_3)_2Cp}_2(\mu\text{-NCCHCN})][PF_6]$ (3)

A mixture of 2 (870 mg, 1.08 mmol) and [Ru(NC-Me)(PPh₃)₂Cp][PF₆] (940 mg, 1.08 mmol) was heated in refluxing thf (60 ml) for 90 min. The cooled yellow solution was slowly added to rapidly stirred hexane (300 ml) to give a fine yellow precipitate that was collected and dried to give $[{Cp(PPh_3)_2Ru}_2(\mu -$ NCCHCN)][PF₆] (3) (1.57 g, 91%). Anal. Calc. (C₈₅H₇₁F₆N₂P₅Ru₂): C, 64.07; H, 4.46; N, 1.76; M, 1146. Found: C, 64.07; H, 4.43; N, 1.76%. IR (nujol): v(CN) 2172; v(PF) 838 cm⁻¹. ¹H NMR: δ 7.09–7.28 (m, 60H, Ph), 4.46 (s, 1H, CH), 4.23 (s, 10H, Cp). ¹³C NMR: δ 139.54 (s, Ru-NC), 127.78–136.75 (m, Ph), 82.39 (s, Cp), 9.42 (s, CH). ³¹P NMR: δ 42.11 (s, PPh₃), -143.11 (septet, PF₆). ES mass spectrum (positive ion mode, m/z): 1146, M⁺, 1184, [M – PPh₃]⁺; 922, $[M - 2PPh_3]^+$; 660, $[M - 3PPh_3]^+$.

7.3.4. $Ru\{NCC(CN)_2\}(PPh_3)_2Cp(4)$

A mixture of RuCl(PPh₃)₂Cp (500 mg, 0.69 mmol) and KC(CN)₃ (89 mg, 0.69 mmol) was heated in refluxing thf/MeOH (1:1, 50 ml) for 1 h. Solvent was removed under vacuum and the solid extracted in the minimum quantity of CH₂Cl₂ and filtered dropwise into rapidly stirred hexane to give a bright yellow precipitate of Ru{NCC(CN)₂}(PPh₃)₂Cp (4) (526 mg, 97%). IR (nujol): v(CN) 2172 cm⁻¹. ¹H NMR: δ 7.03–7.31 (m, 30H, Ph), 4.28 (s, 5H, Cp). ¹³C NMR: δ 133.37 (s, NC-Ru), 127.88-136.65 (m, Ph), 118.74 (s, CN), 82.35 (s, Cp), 11.29 (s, C). ³¹P NMR: δ 41.45 (s, PPh₃). ES mass spectrum (positive ion mode, m/z): 1472, [{Ru(PPh₃)₂- $Cp_{2}C(CN)_{3}^{+};$ 1209, $[{Ru(PPh_3)_2Cp}_2C(CN)_3 P-Ph_3$]⁺; 948, [{Ru(PPh_3)_2Cp}_2C(CN)_3 - 2PPh_3]⁺; 691, $[Ru(PPh_3)_2-p]^+$. Lit. values [6]: IR (nujol) 2175 cm⁻¹; ¹H NMR (CDCl₃): δ 7.21–7.30 (Ph), 4.29 (Cp); ¹³C NMR (CDCl₃): 128.5–136.4 (Ph), 82.8 (Cp).

7.3.5. $[{Ru(PPh_3)_2Cp}_2(NC)_2C(CN)][PF_6]$ (5)

A mixture of 4 (400 mg, 0.51 mmol), RuCl(PPh₃)₂Cp (372 mg, 0.51 mmol) and NH₄PF₆ (84 mg, 0.51 mmol) in MeOH/thf (1:1, 40 ml) was heated at reflux point for 3 h.

Solvent was removed under vacuum and the solid was extracted in the minimum amount of CH_2Cl_2 and added dropwise to rapidly stirred hexane to give yellow [{Ru(PPh_3)_2Cp}_2{(μ -NC)_2C(CN)}][PF_6] (5) (750 mg, 91%). Anal. Calc ($C_{86}H_{38}F_6N_3P_5Ru_2$): C, 63.89; H, 4.36; N, 2.59; M (cation), 1472. Found: C, 63.29; H, 4.50; N, 2.55%. IR (nujol): ν (CN) 2204, 2189 cm⁻¹. ¹H NMR: δ 7.03–7.31 (m, 60H, Ph), 4.34 (s, 10H, Cp). ¹³C NMR: δ 130.01 (s, NC-Ru), 128.08–136.51 (m, Ph), 83.04 (s, Cp), 15.89 (s, C). ³¹P NMR: δ 41.54 (s, PPh₃), -143.12 (septet, PF₆). ES mass spectrum (positive ion mode, *m*/*z*): 1472, M⁺; 1210, [M – PPh₃]⁺; 948, [M – 2PPh_3]⁺; 691, [Ru(PPh_3)_2Cp]⁺.

7.3.6. $Ru\{N=C=C(CN)C(CN)=C(CN)_2\}(PPh_3)_2Cp$ (6)

A suspension of RuCl(PPh₃)₂Cp (500 mg, 0.69 mmol) and [NMe₄][C₃(CN)₅] (166 mg, 0.69 mmol) in methanol (15 ml) was heated at reflux point for 1 h. Solvent was removed and the bright red residue was chromatographed (alumina, 20 × 2 cm column, CH₂Cl₂/Et₂O 1/2). The bright orange fraction was collected, evaporated and dissolved in the minimum amount of CH₂Cl₂. Dropwise addition to stirred hexane gave bright orange Ru{N=C=C(CN)C(CN)=C(CN)₂}(PPh₃)₂Cp (**6**) (490 mg, 83%). Anal. Calc. (C₄₉H₃₅N₅P₂Ru): C, 68.70; H, 4.10; N, 8.20; M, 857. Found: C, 68.70; H, 4.11; N, 8.09%. IR (nujol): ν (CN) 2199 cm⁻¹. ES mass spectrum (positive ion mode, *m*/*z*): 1548, [{Ru(PPh₃)₂Cp}₂-C₃(CN)₅]⁺; 1286, [{Ru(PPh₃)₂Cp}₂C₃(CN)₅ – PPh₃]⁺, 1024, [{Ru(PPh₃)Cp}₂C₃(CN)₅ – 2PPh₃]⁺; 691, [Ru-(PPh₃)₂Cp]⁺; 430, [Ru(PPh₃)Cp]⁺.

The ¹H and ¹³C NMR spectra showed the presence of two isomers in solution in 5/2 ratio. Major isomer: ¹H NMR: δ 7.07–7.34 (m, 30H, Ph), 4.52 (s, 5H, Cp). ¹³C NMR: δ 128.26–135.92 (m, Ph), 124.86 (s, Ru-NC), 115.48, 114.93, 114.14, 113.28 (4×s, CN), 83.47 (s, Cp), 60.54, 57.75 [2×s, *C*(CN)₂]. ³¹P NMR: δ 41.39 (s, PPh₃). Minor isomer: ¹H NMR: δ 7.07–7.34 (m, 30H, Ph), 4.40 (s, 5H, Cp). ¹³C NMR: δ 128.26–135.92 (m, Ph), 124.86 (s, Ru-NC), 115.54, 114.32, 112.51, 112.06 (4×s, CN), 83.47 (s, Cp), 62.15, 57.70 [2×s, *C*(CN)₂]. ³¹P NMR: δ 41.06 (s, PPh₃).

7.3.7. $[{Ru(PPh_3)_2Cp}_2{\mu-[N=C=CN]_2C(CN)}][PF_6] (7)$

A suspension of RuCl(PPh₃)₂Cp (500 mg, 0.69 mmol), [NMe₄][C₃(CN)₅] (82 mg, 0.34 mmol) and NH₄PF₆ (112 mg, 0.69 mmol) in methanol (25 ml) was heated at reflux point for 30 min. Solvent was removed and the dark purple solid was chromatographed (20 cm alumina column). Elution with acetone/hexane (3/7) gave a bright orange band containing **6** (52 mg, 9%). The major band was eluted with acetone–hexane (1/1) to give red [{Ru(PPh₃)₂Cp}₂{ μ -[N=C=C(CN)]₂-C(CN)}][PF₆] (7) (490 mg, 77%). Anal. Calc. (C₉₀H₇₀F₆N₅P₅Ru₂): C, 63.86; H, 4.16; N, 4.13; M

(cation), 1548. Found: C, 63.75; H, 4.24; N, 4.06%. IR (nujol): v(CN) 2192, 2204; $v(PF_6)$ 837 cm⁻¹. ES mass spectrum (positive ion mode, m/z): 1548, [{Ru(PPh_3)_2-Cp}_2C_3(CN)_5]⁺; 1286, [{Ru(PPh_3)_2Cp}_2C_3-(CN)_5 - PPh_3]⁺, 1024, [{Ru(PPh_3)Cp}_2C_3(CN)_5]⁺; 691, [Ru(PPh_3)_2Cp]⁺; 429, [Ru(PPh_3)Cp]⁺.

The NMR spectra of 7 showed the presence of three species in solution (Table 1). In the ¹³C NMR spectrum, the following peaks could not be individually assigned: δ 128.32–135.86 (m, Ph), 111.24, 112.57, 113.89, 114.19, 114.58, 115.18, 115.90 (7 × s, CN).

7.3.8. $Ru\{N = C = C(CN)C(CN)C(CN)_2\}(dppe)Cp^*(\mathbf{8})$

A mixture of RuCl(dppe)Cp* (100 mg, 0.15 mmol) and $[NMe_4][C_3(CN)_5]$ (35 mg, 0.15 mmol) were stirred in MeOH (10 ml) at r.t. for 1 h. Solvent was removed and the bright orange residue was chromatographed (20 cm silica-gel column, acetone/hexane 35/65). The bright orange band was evaporated, extracted into the minimum of CH₂Cl₂ and precipitated by hexane to give Ru{N=C=C(CN)C(CN)C(CN)₂}(dppe)Cp* (8) (92 mg, 76%). Anal. Calc. (C₄₄H₃₉N₅P₂Ru): C, 65.91; 4.86; N, 8.74; M, 801. Found: C, 65.79; H, 4.84; N, 8.69%. IR (nujol): v(CN): 2168, 2191, 2211 cm⁻¹. ES mass spectrum (positive ion mode, *m*/*z*): 1437, [{Ru(dppe)Cp*}₂C₃(CN)₅]⁺; 802, [Ru{C₃(CN)₅}(dppe)Cp*]⁺; 635, [Ru(dppe)Cp*]⁺.

The ¹H and ¹³C NMR spectra showed the presence of two isomers in solution in 5/2 ratio. Major isomer: ¹H NMR: δ 7.22–7.54 (m, 20H, Ph), 2.2–2.9 (m, 4H, CH₂), 1.46 [t, ³J(HP) = 1.5 Hz, 15H, Cp*]. ¹³C NMR: δ 128.27–135.81 (m, Ph), 124.11 (s, Ru-NC), 115.61, 113.30, 112.67, 112.25 (4×s, CN), 92.37 (s, Cp*), 59.98, 57.51 [2×s, *C*(CN)₂], 28.28 [t, ¹J(CP) = 22.3 Hz, CH₂], 9.48 (s, Cp*). ³¹P NMR: δ 74.98 (s, dppe). Minor isomer: ¹H NMR: δ 7.22–7.54 (m, 20H, Ph), 2.2–2.9 (m, 4H, CH₂), 1.44 [t, ³J(HP) = 1.8 Hz, 15H, Cp*]. ¹³C NMR: δ 128.26–135.92 (m, Ph), 121.87 (s, Ru-NC), 115.61, 115.30, 113.30, 112.95 (4×s, CN), 92.76 (s, Cp), 57.98, 57.36 [2×s, *C*(CN)₂], 29.27 [t, ¹J(CP) = 22.34 Hz, CH₂], 9.48 (s, Cp*). ³¹P NMR: δ 76.88 (s, dppe).

7.3.9. $[{Ru(dppe)Cp^*}_2{\mu[N=C=C(CN)]_2C(CN)}]-[PF_6] (9)$

A mixture of RuCl(dppe)Cp* (100 mg, 0.15 mmol), [NMe₄][C₃(CN)₅] (18 mg, 0.075 mmol) and NH₄PF₆ (25 mg, 0.15 mmol) was stirred in MeOH (10 ml) at r.t. for 1 h. Solvent was removed and the dark purple residue chromatographed (20 cm silica gel column). Elution with acetone/hexane (35/65) gave **8** (13 mg, 11%). The purple fraction eluted with acetone/hexane (1/1) contained [{Ru(dppe)Cp*}₂{ μ [N=C=C(CN)]₂C-(CN)}][PF₆] (**9**) (88 mg, 74%). Anal. Calc. (C₈₀H₇₈F₆-N₅P₅Ru₂): C, 60.79; H, 4.97; M (cation), 1437. Found: C, 61.09; H, 5.12%. IR (nujol): ν (CN) 2213, 2195, 2186, 2179, $v(PF_6)$ 835 cm⁻¹. ES mass spectrum (positive ion mode, *m/z*): 1437, [{Ru(dppe)Cp*}₂C₃(CN)₅]⁺; 635 [Cp(dppe)Ru]⁺.

The NMR spectra of **9** showed the presence of three species in solution (Table 1). In the ¹³C NMR spectrum, the following peaks could not be individually assigned: δ 128.12–135.32 (m, Ph), 107.25, 111.55, 112.78, 112.94, 113.08, 115.10, 115.55, 115.77 (8 × s, CN); 28.04–29.65 (m, CH₂).

7.3.10. $\{Ru(PPh_3)_2Cp[\mu-NCC\{C(CN)=C(CN)_2\}-CN]\}_2$ (10)

A solution of **6** (100 mg, 0.12 mmol) was heated in refluxing toluene (50 ml) for 12 h. Solvent was removed and the residue was purified by preparative TLC plates using chloroform as the solvent. A bright red band (R_f 0.6) was collected and after replating afforded {Ru(PPh_3)_2Cp [μ -NCC{C(CN)=C(CN)_2CN]}_2 (**10**) (8 mg, 11%). Anal. Calc. (C₆₂H₄₀N₁₀P₂Ru₂): C, 62.52; H, 3.36; N, 11.76; M, 1190. Found: C, 62.59; H, 3.30; N, 11.74%. IR (nujol): ν (CH₂Cl₂): 2209, 2189 cm⁻¹. ES mass spectrum (with NaOMe, *m/z*): 1213, [M + Na]⁺; 1024, [M - C₃(CN)₅]⁺.

The NMR spectra (Table 1) showed the presence of four isomers in solution. Other peaks: ¹H NMR: δ 7.34–7.48 (m, 30H, Ph). ¹³C NMR: δ 121.46, 124.04 [isomer 1, C(3)], 121.07, 124.42 [isomer 2, C(3)], 132.88 [isomer 1, C(1)], 132.73, 132.93 [isomer 2, C(1)], 112.84, 112.89, 113.13, 114.88 (4×s, CN), 128.52–133–83 (m, Ph). ³¹P NMR: δ 49.86 (s). Minor isomer: ¹H NMR: $\delta_{\rm H}$ 7.34–7.48 (m, 30H, Ph), 4.58 (s, 5, Cp), 4.47 (s, 5, Cp). ³¹P NMR: δ 51.04 (s), 48.74 (s).

7.4. Structure determinations

Full spheres of data to $2\theta = 58^{\circ}$ were measured at ca 153 K using a Bruker AXS CCD area-detector instrument, merged to unique sets after "empirical"/multiscan absorption corrections, N_{tot} data merging to N unique (R_{int} quoted), N_0 with $F > 4\sigma(F)$ being used in the refinements. All data were measured using monochromatic Mo K α radiation, $\lambda = 0.7107_3$ Å. In the refinements, anisotropic thermal parameter forms were used for the non-hydrogen atoms, $(x, y, z, U_{iso})_{H}$ being constrained at estimated values. Conventional residuals R, R_w on |F| are quoted, weights being $[\sigma^2(F) + 0.0004F^2]^{-1}$. Neutral atom complex scattering factors were used; computation used the XTAL 3.4 program system [32]. Pertinent results are given in Figs. 2-4 (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and Tables 2, 3 and 5.

In a number of the determinations, specimen quality and disorder presented significant difficulties, impacting adversely on the precision of the determinations. Specific variations in procedure:

2. The solvent dichloromethane (molecule 2) was modelled as disordered over two sets of sites, accupan-

Crystal data and refine	ement details					
Compound	2	3	4	8	6	10
Formula	$\mathrm{C}_{44}\mathrm{H}_{36}\mathrm{N}_{2}\mathrm{P}_{2}\mathrm{Ru}\cdot\mathrm{CH}_{2}\mathrm{Cl}_{2}$	$\mathbf{C_{85}H_{71}F_6N_2P_5Ru_2}\cdot 3\mathbf{C_7H_8}$	$\mathrm{C}_{45}\mathrm{H}_{35}\mathrm{N}_3\mathrm{P}_2\mathrm{Ru}\cdot\sim\!\!0.7\mathrm{CHCl}_3$	$\mathrm{C}_{44}\mathrm{H}_{39}\mathrm{N}_{5}\mathrm{P}_{2}\mathrm{Ru}$	$\mathrm{C_{80}H_{78}F_6N_5P_5Ru_2} \cdot 0.5\mathrm{CH_2Cl_2}$	$C_{62}H_{40}N_{10}P_2Ru_2$
MW	840.7	1867.9	864.4	800.9	1623.0	1189.2
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	11.1273(9)	13.091(3)	10.680(1)	13.9230(8)	15.362(5)	14.382(2)
$b(\mathbf{\hat{A}})$	16.765(1)	46.79(1)	22.278(2)	14.812(1)	11.466(4)	9.364(2)
c (Å)	41.818(3)	15.012(4)	17.329(1)	19.025(1)	41.564(14)	20.582(2)
β (°)	95.310(1)	105.967(4)	98.980(1)	93.637(1)	94.026(7)	108.521(3)
$V(\text{Å}^3)$	7768	8840	4073	3915	7303	2628
Ζ	8	4	4	4	4	2
$D_{ m c}~({ m g~cm^{-3}})$	1.43_{8}	1.40_{3}	1.41_0	1.35_{8}	1.47_{6}	1.50_{2}
$\mu \ (\mathrm{cm}^{-1})$	6.6	5.0	6.4	5.2	6.2	6.9
Crystal size (mm)	$0.15 \times 0.14 \times 0.10$	$0.28 \times 0.12 \times 0.11$	$0.55 \times 0.45 \times 0.35$	$0.35 \times 0.16 \times 0.13$	$0.32 \times 0.13 \times 0.04$	$0.08 \times 0.06 \times 0.03$
$T_{ m min/max}$	0.65	0.92	0.83	0.89	0.79	0.93
$2\theta_{\max}$ (°)	58	52	58	68	46	58
$N_{ m tot}$	86536	54927	46733	58582	56241	26768
$N\left(R_{ m int} ight)$	19765 (0.048)	15405 (0.064)	10192 (0.030)	15375 (0.032)	9898 (0.14)	6818 (0.071)
$N_{ m o}$	14 63 7	11 152	7820	10817	4635	3933
R	0.064	0.081	0.050	0.044	0.10	0.047
R_w	0.073	0.124	0.069	0.050	0.15	0.043
$ \Delta ho_{ m max} $ (e Å ⁻³)	1.73(6)	1.86(7)	1.15(4)	2.3(2)	1.7(2)	0.93(9)

cies refining to 0.713(5) and complement. C,N in the cyano-ligand were assigned in molecule 1 on the basis of refinement behaviour and geometries, the hydrogen on C(1) being refinable in (x, y, z, U_{iso}) ; the same ligand in molecule 2 is oriented differently with high displacement parameters (isotropic) on C(2) and beyond unrealistically large and presumably a foil for disorder, each ligand lying in association with a solvent molecule, disordered in the latter case.

3. The question of disorder and its nature, e.g., the possibility of co-crystallisation of closely related species, is raised more seriously here. Ru(1) and associated ligands, together with the PF_6^- anion refine convincingly and unproblematically, these moieties comprising layers disposed about y = 0.25, 0.75. Displacement parameters of N(2), Ru(2), C(201–205) and two of the three solvent molecules are high, but with no resolution of associated disorder; the two PPh₃ ligands from the P atom and beyond are modelled in terms of superimposed displaced components of equal occupancy, these being disposed about y = 0.5, together with solvent 3, modelled as a rigid body.

4. *T* was 300 K for this study. The occupancy of the $CHCl_3$, despite hydrogen-bonding to the cyano-ligand, refined only to 0.705(4).

9. Weak and limited data would permit meaningful anisotropic displacement parameter refinement for Ru, P, F only. The central ligand was modelled as disordered over a pair of sites of equal occupancy.

10. Somewhat similar disorder was resolved in the central ligand, the two components refining to occupancies of 0.63(1) and complement, the inner, ordered part of the ligand lying close to and parallel with, one of the Ph rings.

7.5. *Ab initio Hartree–Fock and density functional theory calculations*

Quantum chemical ab initio calculations were performed using GAMESS-US [33] at the restricted Hartree–Fock level of theory with the in-built SBKJC effective core potential-containing basis set [34–36]. The number of core electrons replaced with appropriate core potential functions for each atom type are: C = 2, N = 2, P = 10, Ru = 28. All calculations were performed on an Intel-based Beowulf computing cluster [37]. The representation of the models used MOLDEN [38].

Density functional theory calculations using the Amsterdam Density Functional (ADF) package [39] with the Becke–Perdew function were carried out on hydrogenated model complexes (Cp, PH₃ and dHpe in place of Cp*, PPh₃ and dppe) to reduce computational effort. The atomic basis sets used were a double-Slater-type orbital (STO) (ADF basis set II) for C, P, H of the Cp, PH₃ and dHpe ligands, and a triple-Slater-type orbital (STO) + single-STO set (ADF Basis set IV) for the rest

Table 5

of the molecule, with a frozen core approximation for the orbitals up to 1s for C and N, 2p for P and 4p for Ru.

8. Supplementary material

Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC 237211–237216 (complexes 2–4 and 8–10, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk).

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References

- [1] See H.M. Powell, Proc. Chem. Soc. (1959) 73.
- [2] (a) T. Sheng, R. Appelt, V. Comte, H. Vahrenkamp, Eur. J. Inorg. Chem. (2003) 3731;
 (b) H. Vahrenkamp, A. Geiss, G.N. Richardson, J. Chem. Soc.,

Dalton Trans. (1997) 3643; C = 1 + 1 + 1 + 2 = 1 + 2

(c) K.R. Dunbar, R.A. Heintz, Prog. Inorg. Chem. 45 (1997) 283;
(d) W.P Fehlhammer, M. Fritz, Chem. Rev. 93 (1993) 1243.

[3] (a) V. Marvaud, C. Decroix, A. Scuiller, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer, Chem. Eur. J. 9 (2003) 1677;

(b) V. Marvaud, C. Decroix, A. Scuiller, F. Tuyras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer, Chem. Eur. J. 9 (2003) 1692.

[4] C. Bartel, P. Botschwina, H. Bürger, A. Guarnieri, Ä. Heyl, A. Huckauf, D. Lentz, T. Merzliak, E.B. Mkadmi, Angew. Chem. 110 (1998) 3036;
C. Bartel, P. Botschwina, H. Bürger, A. Guarnieri, Ä. Heyl, A.

Huckauf, D. Lentz, T. Merzliak, E.B. Mkadmi, Angew. Chem., Int. Ed. 37 (1998) 2879.

- [5] K.-H. Trylus, U. Kernbach, I. Brüdgam, W.P. Fehlhammer, Inorg. Chim. Acta 291 (1999) 266.
- [6] G.J. Baird, S.G. Davies, S.D. Moon, S.J. Simpson, R.H. Jones, J. Chem. Soc., Dalton Trans. (1985) 1479.
- [7] (a) A. Geiss, H. Vahrenkamp, Inorg. Chem. 39 (2000) 4029;
 (b) A. Geiss, M.J. Kolm, C. Janiak, H. Vahrenkamp, Inorg. Chem. 39 (2000) 4037;

(c) N. Zhu, R. Appelt, H. Vahrenkamp, J. Organomet. Chem. 565 (1998) 187;

(d) A. Geiss, M. Keller, H. Vahrenkamp, J. Organomet. Chem. 541 (1997) 441.

[8] (a) L.-Y. Zhang, J.-L. Chen, L.-X. Shi, Z.-N. Chen, Organometallics 21 (2002) 5919; (b) Z.N. Chen, R. Appelt, H. Vahrenkamp, Inorg. Chim. Acta 309 (2000) 65.

- [9] Y. Zhao, M. Hong, W. Su, R. Cao, Z. Zhou, A.S.C. Chan, J. Chem. Soc., Dalton Trans. (2000) 1685.
- [10] (a) K.M. Anderson, N.G. Connelly, N.J. Goodwin, G.R. Lewis, M.T. Moreno, A.G. Orpen, A.J. Wood, J. Chem. Soc., Dalton Trans. (2001) 1421;
 (b) N.G. Connelly, O.M. Hicks, G.R. Lewis, A.G. Orpen, A.J. Wood, J. Chem. Soc., Dalton Trans. (2000) 1637;
 (c) N.G. Connelly, G.R. Lewis, M.T. Moreno, A.G. Orpen, J. Chem. Soc., Dalton Trans. (1998) 1905;
 (d) N.G. Connelly, O.M. Hicks, G.R. Lewis, M.T. Moreno, A.G. Orpen, J. Chem. Soc., Dalton Trans. (1998) 1913.
- [11] (a) P. Braunstein, B. Oswald, A. Tiripicchio, F. Ugozzoli, J. Chem. Soc., Dalton Trans. (2000) 2195;
 (b) P. Braunstein, B. Oswald, A. Tiripicchio, M. Tiripicchio-Camellini, Angew. Chem. 102 (1990) 1206;
 (c) P. Braunstein, B. Oswald, A. Tiripicchio, M. Tiripicchio-Camellini, Angew. Chem., Int. Ed. Engl. 29 (1990) 1140.
- [12] A. Maiboroda, H. Lang, New J. Chem. 25 (2001) 642.
- [13] A.I.F. Venâncio, M.L. Kuznetsov, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, Inorg. Chem. 41 (2002) 6456.
- [14] (a) J.S. Miller, Inorg. Chem. 39 (2000) 4392;
 (b) J.S. Miller, A.J. Epstein, Coord. Chem. Rev. 205–206 (2000) 651.
- [15] S. Duclos, F. Conan, S. Triki, Y. Le Mest, M.L. Gonzalez, J.S. Pala, Polyhedron 18 (1999) 1935.
- [16] C. Diaz, I. Izquierdo, M.L. Valenzuela, N. Yutronic, Inorg. Chem. Commun. 3 (2000) 525.
- [17] (a) W.J. Middleton, E.L. Little, D.D. Coffman, V.A. Engelhardt, J. Am. Chem. Soc. 80 (1958) 2795;
 (b) D.A. Dixon, W.B. Farnham, W.B. Middleton, D.C. Roe, F. Davidson, B.E. Smart, J.S. Miller, J. Phys. Chem. 92 (1988) 2137;
 (c) L.R. Melby, in: Z. Rappoport (Ed.), The Chemistry of the Cyano Group, Wiley, New York, 1970, p. 639;
 (d) A. Fatiadi, Synthesis (1987) 959.
- [18] M.I. Bruce, R.C. Wallis, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1981) 2205.
- [19] M.I. Bruce, P.J. Low, B.W. Skelton, A.H. White, New J. Chem. 22 (1998) 419.
- [20] (a) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949;
 (b) M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, Organometallics 22 (2003) 3184.
- [21] R.L. Cordiner, D. Corcoran, D.S. Yufit, A.E. Goeta, J.A.K. Howard, P.J. Low, Dalton Trans. (2003) 3541.
- [22] T.J. Johnson, M.R. Bond, R.D. Willett, Acta Crystallogr. C 44 (1988) 1890.
- [23] L.-Y. Zhang, L.-X. Shi, Z.-N. Chen, Inorg. Chem. 42 (2003) 633.
- [24] (a) W. Kaim, M. Moscherosch, Coord. Chem. Rev. 129 (1994) 157;
 (b) W.H. D. Liller, L. C. Lin, A. (1997) 2 (1998) 7.
- (b) W.H. Baddley, Inorg. Chim. Acta Rev. 2 (1968) 7;
 (c) H. Köhler, Z. Chem. 13 (1973) 401.
 (a) T. Naota, A. Tanna, S. L. Murahashi, L. Am. Chem. S.
- [25] (a) T. Naota, A. Tanna, S.-I. Murahashi, J. Am. Chem. Soc. 122 (2000) 2960;
 (b) T. Naota, A. Tannna, S. Kamuro, S.-I. Murahashi, J. Am. Chem. Soc. 124 (2002) 6842.
- [26] (a) H.P. Xia, W.F. Wu, W.S. Ng, I.D. Williams, G. Jia, Organometallics 16 (1997) 2940;
 (b) H.P. Xia, W.S. Ng, J.S. Ye, X.-Y. Li, W.T. Wong, Z. Lin, C. Yang, G. Jia, Organometallics 18 (1999) 4552.
- [27] M.I. Bruce, P.J. Low, Adv. Organomet. Chem. 50 (2004) 179.
- [28] F. Coat, F. Paul, C. Lapinte, L. Toupet, K. Costuas, J.-F. Halet, J. Organomet. Chem. 683 (2003) 368.
- [29] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, J. Chem. Soc., Dalton Trans. (1998) 519.

- [30] N.G. Connelly, W.G. Geiger, Chem. Rev. 96 (1996) 877.
- [31] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, Inorg. Synth. 28 (1990) 270.
- [32] XTAL 3.4: S.R. Hall, G.S.D. King, J.M. Stewart, The XTAL 3.4 Users' Manual, University of Western Australia, Perth, 1995.
- [33] GAMESS-US, June 2002 release. Available from http:// www.msg.ameslab.gov/GAMESS/.html M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen S. Koseki, N. Matunaga, K.A. Nguyen, S.J. Su, T.L. Windus M. Duouis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
- [34] W.J. Stevens, H. Basch, M. Krauss, J. Chem. Phys. 81 (1984) 6026.
- [35] W.J. Stevens, H. Basch, M. Krauss, P. Jasien, Can. J. Chem. 70 (1992) 612.
- [36] T.R. Cundari, W.J. Stevens, J. Chem. Phys. 98 (1993) 5555.
- [37] K.A. Hawick, D.A. Grove, P.D. Coddington, M.A. Buntine, Internet J. Chem. 4 (2000) 3.
- [38] G. Schaftenaar, J.H. Noordik, J. Comput. Aided Mol. Design 14 (2000) 123.
- [39] Amsterdam Density Functional Program, ADF 2003.01, SCM, Vrije Universiteit, Amsterdam, The Netherlands, 2003. Available from http://www.scm.com.