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Synthesis, structural and electronic characterisation of *trans*-[$OsCl_2(PEt_2Ph)_3\{(NC)_2C{=}C(CN)OH\}$], a complex featuring a redox-active, tetracyanoethylene-derived ligand‡

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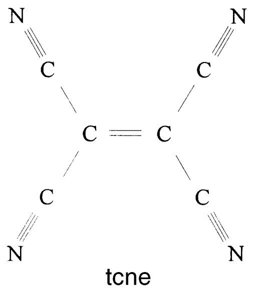
Reaction of *mer*-[$OsCl_3(PEt_2Ph)_3$] with $AgBF_4$ and tetracyanoethylene (tcne) in tetrahydrofuran yielded the unexpected product *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)], where tcva is tricyanovinyl alcohol (1,1,2-tricyano-2-hydroxyethylene). Structural characterisation of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] was accomplished through IR spectroscopy, fast atom bombardment mass spectrometry, elemental analysis and single-crystal X-ray diffraction. The crystallographic study revealed that tcva is σ-bound to the Os atom *via* nitrogen and that the OH group occupies the *cis* position with respect to the metal-bound nitrogen. The frontier orbitals of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] were investigated by electrochemistry and UV/VIS, IR and EPR spectroelectrochemical studies, which revealed that the complex is best described as *trans*-[$Os^{II}Cl_2(PEt_2Ph)_3(tcva)^0$].

The co-ordination chemistry of tetracyanoethylene (tcne) and 7,7,8,8-tetracyanoquinodimethane (tcnq) have been the source of much interest in recent years.[1] They are potent electron acceptors and their reactions with transition-metal complexes exhibit considerable diversity of structural form and electronic interactions. The products of these reactions may be divided into several categories: (*i*) salts, in which the tetranitrile is present as a counter anion.[2–5] The electron-accepting properties of tcne and tcnq are demonstrated by the existence of species such as [$\{Co(C_5Me_5)_2\}_2$][tcne],[2] in which the tetranitrile is present as a dianion. Ferromagnetism[3,4] and other unusual magnetic and electronic properties[5] have often been observed in such species. (*ii*) Charge-transfer complexes, in which electron transfer from metal to tetranitrile is incomplete. Perhaps the best known example of such a species is [$Fe(C_5H_5)_2$·tcne].[6] One feature of interest in both salts and charge-transfer complexes of tcne/q is the tendency to form low-dimensional solids, in which the physical properties show an unusually high degree of anisotropy.[4,7] (*iii*) Metal–alkene bound π complexes. This has been the most widely reported form of bonding between tcne and transition-metal complexes.[1,8] As a result of the electron-withdrawing CN groups, there is usually considerable back bonding from the metal to the alkene π* orbital. In general, the planarity of the tetranitrile ligand is lost, and considerable lengthening of the alkene double bond is observed.[8] (*iv*) Metal–nitrogen bound σ complexes. In this mode of co-ordination, tcne/q may bind as a neutral or anionic[9] ligand. Species featuring 'intermediate oxidation states',[10] or containing both the neutral and the anionic tetranitrile,[11] have also been reported. The compounds tcne/q may also act as bridging ligands, providing a conjugated link between two or more metal centres.[12,13] Ligand geometries tend to be similar to those observed in the analogous oxidation state of the unbound tetranitrile and, in the solid state, ligand 'stacking' is often observed.[9,10,13,14] (*v*) Complexes in which tcne has reacted with other ligands. Insertions into metal–ligand bonds (usually into M−H, M−C or M−N bonds), 2 + 2 and 2 + 4 cycloaddition reactions (tcne is an excellent dienophile) and rearrangement reactions are the most commonly reported examples of this phenomenon.[15] Occasionally, species are reported in which interactions between the metal centre and tcne/q fall into more than one of the above categories.[1,16]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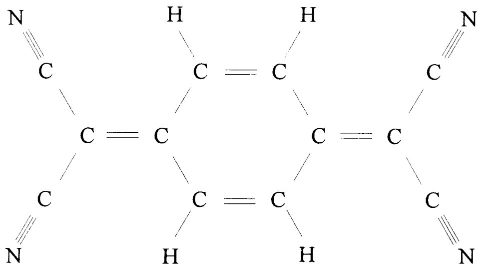
tcnq

Complexes of general formula [$OsX_3(PR_2R')_3$] (X = Cl or Br; R, R′ = alkyl or aryl groups and may be equivalent) appear to be well suited to reactions with a strong π-acceptor ligand such as tcne or tcnq. Halide loss is readily induced (usually by reduction of the starting complex), and the resultant species reacts with various compounds usually giving complexes of formula [$OsX_2(PR_2R')_3L]^{n+}$ or [$OsX_2(PR_2R')_2L_2]^{n+}$ (L = dmf, PhCN, MeCN, N_2, CO, PR_3, *etc.*).[17,18] In general, the product complexes contain Os^{II}. It is possible to induce such reactions by either chemical[17] or electrosynthetic[18] methods, although it has been found that the stereochemistry of the product may depend on the methods employed. In cases where *mer*-[$OsX_2(PR_2R')_3L]^{n+}$ is obtained the *trans*-X_2 isomer is usually the kinetically favoured product, but the *cis*-X_2 isomer tends to have greater thermodynamic stability.[18]

We report here the reaction of *mer*-[$OsCl_3(PEt_2Ph)_3$] with tcne, which results in the formation of the unexpected product *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] [tcva = tricyanovinyl alcohol (1,1,2-

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‡ *Supplementary data available* (No. SUP 57238, 2 pp.): fast atom bombardment mass spectrometry data for *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

tricyano-2-hydroxyethylene)]. The structural and electronic characterisation of this product are reported and discussed.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 598 IR spectrometer, UV/VIS/NIR spectra on a Perkin-Elmer Lambda-9 spectrophotometer, spectroelectrochemical studies being conducted within an optically transparent electrode cell,[19] EPR spectra were recorded on a Bruker ER-200D-SRC spectrometer, using an *in situ* spectroelectrochemical cell.[19] In both UV/VIS/NIR and EPR spectroelectrochemical studies, the potential source was a Metrohm E506 potentiostat. Infrared spectroelectrochemical studies involved electrosynthesis in a conventional coulometric cell and transfer of the electrogenerated species to solution IR cells. Voltammetric and coulometric studies were conducted using a PAR-170 electrochemistry system, and were recorded on a Hewlett-Packard 7045A X-Y recorder. All electrochemical experiments were conducted with $[NBu^n_4][BF_4]$ as supporting electrolyte and the solutions were purged with Ar for 30 min prior to study. Electrochemical experiments were performed using a conventional three-electrode configuration, with Pt micro-working and counter electrodes and a Ag–AgCl reference electrode against which the ferrocene–ferrocenium couple was measured at +0.55 V. Cyclic voltammograms were recorded using a scan rate of 100 mV s^{-1}, while a.c. and stirred voltammograms were recorded at a scan rate of 20 mV s^{-1}. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos-50TC spectrometer, using thioglycerol as the supporting matrix.

Compounds OsO_4, tcne, PEt_2Ph, $AgBF_4$, NBu^n_4OH, HBF_4, silica and HCl were used as supplied, $[NBu^n_4][BF_4]$ was prepared by neutralisation of NBu^n_4OH with HBF_4 in water, the precipitated product being purified by recrystallisation from water and methanol and dried *in vacuo*. Dichloromethane was purified by standing over KOH pellets, then distillation over P_2O_5, under N_2, tetrahydrofuran (thf) was purified by distillation over Na wire and benzophenone, under N_2, hexane was purified by distillation over Na wire, under N_2. Other solvents were used as supplied.

Preparations

***mer*-[OsCl$_3$(PEt$_2$Ph)$_3$].** This complex was prepared by a method similar to that published by Chatt *et al.*[20] Concentrated HCl (1.0 cm^3) and PEt_2Ph (2.00 g, 12.0 mmol) were added, under N_2, to nitrogen-purged ethanol. The compound OsO_4 (1.00 g, 3.93 mmol) was added, and the reaction mixture was heated to reflux for 15 min. After cooling, crude *mer*-$[OsCl_3(PEt_2Ph)_3]$ was obtained by filtration {the main impurity being $[(PEt_2Ph)_3Os(\mu\text{-}Cl)_3Os(PEt_2Ph)_3]^+$}. The product was purified by elution with CH_2Cl_2 from a silica column, in 60% yield. FAB mass spectrum: *m/z* 795, $[C_{30}H_{45}Cl_3OsP_3]^+$ requires *m/z* 795. IR (KBr): 1482m, 1460 (sh), 1451m, 1432s, 1250m, 1100m, 1042s, 1030s, 762m, 752m, 745m, 728s, 704s, 698s cm^{-1}.

***trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)].** The complex *mer*-$[OsCl_3(PEt_2Ph)_3]$ (140 mg, 0.176 mmol) and tcne (45 mg, 0.351 mmol) were dissolved in nitrogen-purged thf (30 cm^3), under N_2. A solution of $AgBF_4$ (40 mg, 0.21 mmol) in thf (10 cm^3) was added, inducing immediate reaction. The reaction mixture was allowed to stand in darkness while the AgCl precipitate settled, then filtered under gravity. The volume of solvent was reduced to approximately 10 cm^3 and the product was precipitated by addition of hexane (25 cm^3), filtered off and washed repeatedly with hexane. The yield of *trans*-$[OsCl_2(PEt_2Ph)_3(tcva)]$ was 120 mg (78%) (Found: C, 48.2; H, 5.3; N, 4.9. Calc. for $C_{35}H_{46}Cl_2N_3OOsP_3$: C, 47.8; H, 5.25; N, 4.8%). FAB mass spectrum: *m/z* 879, 843, 760, 725, 594, 555, 525, 429, 393, 167 (SUP 57238). IR (KBr): 3250m, 2225 (sh), 2220m, 2185m, 1610s, 325m, 310w cm^{-1}.

Overlaying a thf solution of the complex with *n*-hexane resulted in formation of crystals suitable for X-ray diffraction.

Crystallography

Crystallographic data for *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]·0.5-C$_4$H$_8$O. Deep red lath of dimensions 0.16 × 0.25 × 0.54 mm; $C_{37}H_{50}Cl_2N_3O_{1.5}OsP_3$; $M = 919.9$. The space group was determined from θ values of 23 reflections measured at ±ω such that $14 < \theta < 16°$. Monoclinic, space group = $P2_1/n$ (alternate no. 14 of $P2_1/c$), $a = 12.8579(14)$, $b = 18.313(2)$, $c = 17.144(2)$ Å, $\beta = 94.349(11)°$, $Z = 4$, $D_c = 1.509$ g cm^{-3}, $\mu = 34.55$ cm^{-1}, $F(000) = 1840$.

Collection and processing of crystallographic data. The crystal was fixed to a glass fibre and mounted on a Stoe Stadi-4 four-circle diffractometer. Data were collected at 298 K in the ω–2θ mode using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,74$ Å). Of 5446 unique reflections measured ($2.5 < \theta < 22.5$; $h = -13$ to 13, $k = 0$–18 and $l = 0$–18), 4593 data with $F > 4\sigma(F)$ were used in all calculations. An initial correction for absorption was made[21] (maximum and minimum transmission factors 0.4207 and 0.3102 respectively).

Structure solution and refinement were carried out using SHELX 76,[22] the Os atom of the asymmetric unit being located by Patterson synthesis. All other non-hydrogen atoms were located by a process of iterative least-squares refinement (based on *F*) and Fourier-difference synthesis. Scattering factors for Os were obtained from ref. 23, all other scattering factors were inlaid in SHELX 76. All non-hydrogen atoms except for those within the cocrystallised solvent were refined anisotropically. The C atoms of the phenyl rings were constrained as regular hexagons. The H atom of tricyanovinyl alcohol was located, then refined isotropically with the O–H distance restrained. All other H atoms were refined isotropically in fixed, calculated positions. At isotropic convergence, a final absorption correction was made using DIFABS[24] (maximum and minimum corrections 1.188 and 0.913 respectively). The weighting scheme $w^{-1} = \sigma^2(F) + 0.000244F^2$ was found to give satisfactory agreement analyses. At convergence, the final values of *R* and *R'* were 0.026 and 0.038 respectively for 393 parameters, with a goodness of fit index of 1.234. In the final Fourier-difference synthesis the maximum and minimum residual electron densities were 0.58 and −0.44 e $Å^{-3}$ respectively.

Results and Discussion

Upon addition of $AgBF_4$ to solutions of tcne and *mer*-$[OsCl_3(PEt_2Ph)_3]$, in thf or CH_2Cl_2, an immediate colour change from orange to blue-grey is observed. In thf, the reaction mixture then turns red-purple over the next 30 min as *trans*-$[OsCl_2(PEt_2Ph)_3(tcva)]$ is formed. However, in CH_2Cl_2 it is possible to interrupt the reaction at the intermediate stage. The blue-grey intermediate proved to be extremely reactive and has not been fully characterised.

Structural characterisation

Fast atom bombardment mass spectrometry data for *trans*-$[OsCl_2(PEt_2Ph)_3(tcva)]$ shows the molecular ion and various fragments resulting from its breakdown. The elemental analytical data are in good agreement with the calculated composition of *trans*-$[OsCl_2(PEt_2Ph)_3(tcva)]$.

Infrared spectra of *trans*-$[OsCl_2(PEt_2Ph)_3(tcva)]$, recorded as doped KBr discs, show a number of bands in addition to those associated with PEt_2Ph and two Os–Cl stretches at 325 and 310 cm^{-1}. Three CN stretching modes are observed at 2225 (sh), 2220m and 2185m cm^{-1}. More importantly, a broad band corresponding to an O–H stretching vibration is observed at 3250m cm^{-1}. This confirms that the ligand is tricyanovinyl alcohol and not its deprotonated anion. A strong band

Table 1 Selected bond lengths (Å) and angles (°) of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] (estimated standard deviations in parentheses)

Os−N(11)	2.064(4)	C(11T)−C(1T)	1.406(7)
Os−Cl(1)	2.3488(11)	C(1T)−C(12T)	1.451(9)
Os−Cl(2)	2.3448(12)	C(1T)−C(2T)	1.328(9)
Os−P(1)	2.4270(12)	C(12T)−N(12)	1.056(12)
Os−P(2)	2.3763(12)	C(2T)−O(1)	1.178(10)
Os−P(3)	2.4501(12)	C(2T)−C(21T)	1.534(12)
N(11)−C(11T)	1.151(6)	C(21T)−N(22)	1.160(12)
N(11)−Os−Cl(1)	87.92(10)	N(11)−Os−Cl(2)	89.87(10)
N(11)−Os−P(1)	85.32(10)	N(11)−Os−P(2)	177.60(10)
N(11)−Os−P(3)	85.09(10)	Cl(1)−Os−Cl(2)	177.66(4)
Cl(1)−Os−P(1)	88.45(4)	Cl(1)−Os−P(2)	94.46(4)
Cl(1)−Os−P(3)	87.54(4)	Cl(2)−Os−P(1)	92.13(4)
Cl(2)−Os−P(2)	87.75(4)	Cl(2)−Os−P(3)	91.51(4)
P(1)−Os−P(2)	94.99(4)	P(1)−Os−P(3)	169.73(4)
P(2)−Os−P(3)	94.75(4)	Os−N(11)−C(11T)	173.6(4)
N(11)−C(11T)−C(1T)	176.7(5)	C(11T)−C(1T)−C(12T)	114.3(5)
C(11T)−C(1T)−C(2T)	123.8(5)	C(12T)−C(1T)−Cl(2T)	121.6(6)
C(1T)−C(12T)−N(12)	176.4(9)	C(1T)−C(2T)−O(1)	126.7(7)
C(1T)−C(2T)−C(21T)	111.8(6)	O(1)−C(2T)−C(21T)	121.4(7)
C(2T)−C(21T)−N(22)	176.9(9)		

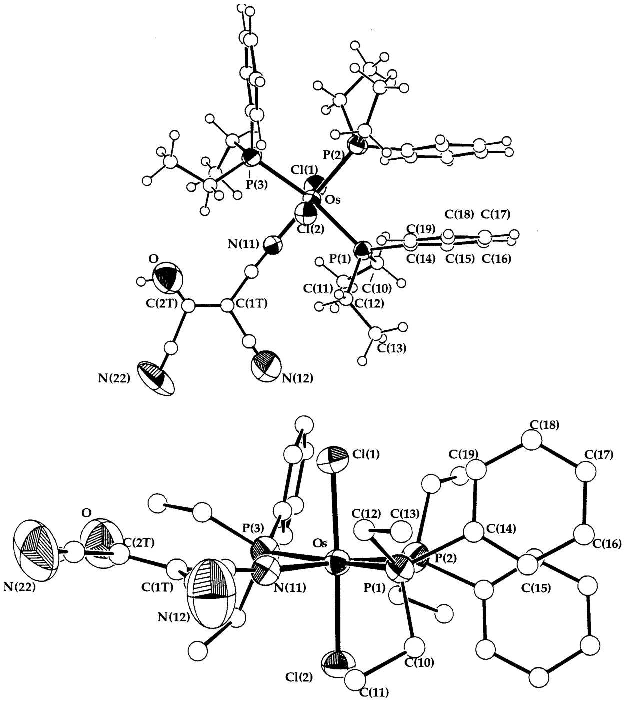

Fig. 1 Views of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]

observed at 1610 cm^{-1} was tentatively assigned as the C=C stretching mode in tcva [in free tcne the C=C stretch is observed in Raman spectra at 1569 cm^{-1} (ref. 25)]. It was found that the energies of the CN stretching modes in *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] are unaffected by dissolution of the complex in CH_2Cl_2.

A single-crystal X-ray diffraction study of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] confirmed its structure, structural data are listed in Table 1. Views of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] are shown in Fig. 1. The complex cocrystallises with thf, with an approximate stoichiometry of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]·0.5 thf. There are four molecules of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] per monoclinic unit cell. As a result of disorder, no distinction has been made between oxygen and the carbon atoms of the cocrystallised thf, and the hydrogen atoms are omitted.

This is the first reported example of metal-bound tricyanovinyl alcohol. The hydroxy group is found to be bound to the olefinic carbon furthest from the metal, *cis* to the Os-bound nitrogen. The structure exhibits a number of other noteworthy features. The Os−N bond is fairly long at 2.064(4) Å, in comparison with other N-bound tcne complexes of osmium. For example, in the complexes [$Os(S_2PR_2)_2(PPh_3)$(tcne)], Os−N = 1.899(7) Å and 1.858(10) Å for R = Me and Ph respectively.[10] The relatively long Os−N bond in *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] is consistent with relatively weak π back bonding from Os to tcva. This is thought to be due, in part, to tcva being *trans* to a phosphine ligand, as opposed to the π donor ligands (such as dithiolates) which occupy the analogous positions in [$Os(S_2PR_2)_2(PPh_3)$(tcne)].

The alkene C=C bond length of the tcva ligand is 1.328(9) Å, which is not significantly different from that observed in free tcne [1.344(3) Å[26]]. The short C=C bond length therefore supports the assignment of the band at 1610 cm^{-1} in the IR spectrum to the alkene stretching mode in tcva. The C=C bond length is also consistent with observations regarding the long Os−N bond length and relatively low π back bonding. It has been shown for tcne complexes that weakening of the C=C bond is related to the extent of back bonding into the tcne π^* lowest unoccupied molecular orbital (LUMO).[1,9,10] Thus, the reported C=C bond in [$Fe(C_5Me_5)_2$][tcne] is 1.392(8) Å,[3] whereas the alkene bond length has increased to 1.49(2) Å in [{$Co(C_5Me_5)_2$}$_2$][tcne].[2] The weakening of the C=C bond in such complexes is most effectively monitored using IR spectroscopy, where the shift of the C=C stretching frequency has been used to assign N-bound tcne complexes as containing anionic tcne.[1,9] Crystallographic data for σ-bound tcne complexes, however, tend to be rather less informative with regard to the relationship between π back bonding and C=C bond lengths. The primary problem is the large uncertainty usually associated with the relevant distance in the reported complexes. For example, in [$Os(S_2PPh_2)_2(PPh_3)$(tcne)], the tcne C=C bond length was found to be 1.401(19) Å,[10] a distance which, because of the large uncertainty associated with it, cannot be said to differ significantly from the corresponding bond length in free tcne.[26] The IR spectrum of [$Os(S_2PPh_2)_2(PPh_3)$(tcne)], however, contains a C=C stretch at 1430 cm^{-1},[10] indicating significant weakening of the olefinic bond.

The C−O bond in *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] is unusually short for a single bond, at 1.178(10) Å. However, this is consistent with structural data for salts of the deprotonated anion of tcva (structural data are not available for free tcva), with reported C−O bond lengths in the range 1.15(2)–1.246(7) Å.[27] The short C−O distance suggests significant interaction between oxygen and the olefinic π orbitals.

The phenyl groups bound to P(1) and P(2) lie in planes which are parallel to within 1.6°. The perpendicular separation of the rings is 3.3 Å and the centre–centre distance is 3.8 Å, suggesting van der Waals interactions similar to those encountered in graphite. Such structural phenomena have been observed previously in arylphosphine complexes of transition metals, *e.g.* [$OsCl_2(PMe_2Ph)_4$].[28] The P atom *trans* to tcva [P(2)] is also significantly closer to Os than P(1) and P(3), possibly as a result of the interaction between the phenyl rings. This proximity is further evidence that tcva is acting as a weak π acceptor in *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)].

Ligand stacking, a fairly common phenomenon in tcne and tcnq complexes,[1,9,10,13,14] is not observed in the crystal structure of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)].

Electronic characterisation

In *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] there are two redox-active sites, the metal centre and the co-ordinated tcva. Given that the related tcne may co-ordinate to a metal centre as a neutral or an anionic ligand, it is clearly important that the interactions of these redox sites be characterised. The structural data suggest that weak electron donation from Os to tcva occurs in *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] [*i.e.* the complex may be described as

Table 2 Data from spectroelectrochemical studies of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]

Species	IR, $\tilde{\nu}$/cm^{-1}	Spectroscopic technique EPR	 UV/VIS, ν/cm^{-1}
trans-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]	2225, 2220, 2185	No signal observed	17 400, 20 400, 32 500, 39 000
trans-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]$^-$	2180, 2140, 2105	$g = 2.012$, $\Delta_{\frac{1}{2}} = 23$ G	24 000, 34 000, 39 500
trans-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]$^+$		No signal observed	13 900, 23 700, 36 000

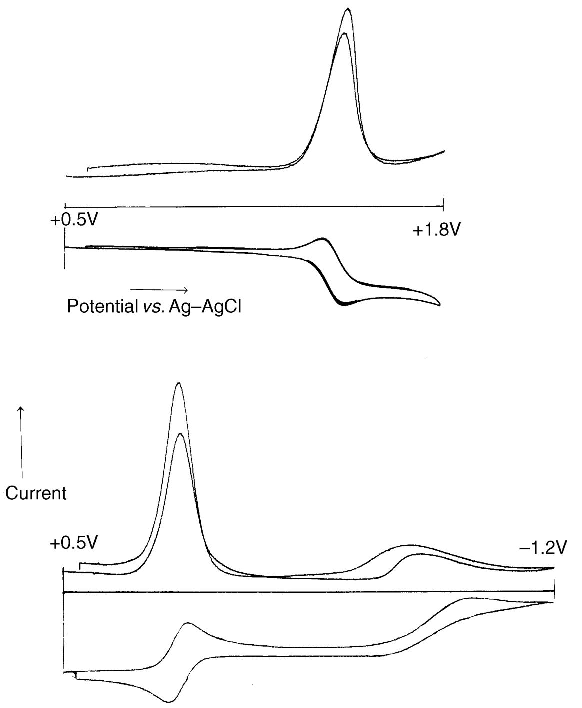

Fig. 2 Cyclic and a.c. voltammograms of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)] in CH$_2$Cl$_2$ at room temperature

Os^{II}(tcva)^0, as opposed to Os^{III}(tcva)$^-$], but electrochemical and spectroelectrochemical studies are required for a rigorous characterisation of the frontier orbitals.

Redox behaviour. The cyclic voltammogram of tcne reveals two reductions. In CH$_2$Cl$_2$, at room temperature, the first reduction is fully reversible and observed at +0.40 V *vs.* Ag–AgCl. The second reduction, at −0.7 V, is only quasi-reversible at room temperature. Unfortunately, no redox data for free tricyanovinyl alcohol are available. The cyclic voltammogram of *mer*-[OsCl$_3$(PEt$_2$Ph)$_3$], in CH$_2$Cl$_2$ at room temperature, reveals a reversible Os$^{III/IV}$ oxidation at +1.05 V, and a partially reversible Os$^{III/II}$ reduction at −0.40 V. The chemically irreversible reduction is associated with the appearance of a redox process at +0.22V which corresponds to the oxidation of the five-coordinate intermediate.

Fig. 2 shows cyclic and a.c. voltammograms of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)] in CH$_2$Cl$_2$ at room temperature. A reversible oxidation is observed at +1.43 V, along with a reversible reduction at +0.09 V and an irreversible reduction at −1.0 V. Coulometric studies reveal that the reversible reduction and oxidation couples are both one-electron processes.

On replacement of a π donor such as Cl$^-$ with a π acceptor ligand, one would predict a large anodic shift in the potential of any metal-based redox processes. It is therefore logical to assign the oxidation at +1.43 V as metal-based. Although redox data are not available for free tcva we suggest that the redox potentials will be comparable with those of tcne. Therefore, we provisionally assign the two reduction processes to be sequential one-electron reductions to the LUMO of tcva. The voltammetric data are therefore generally consistent with relatively weak π back donation from Os into the tcva LUMO.

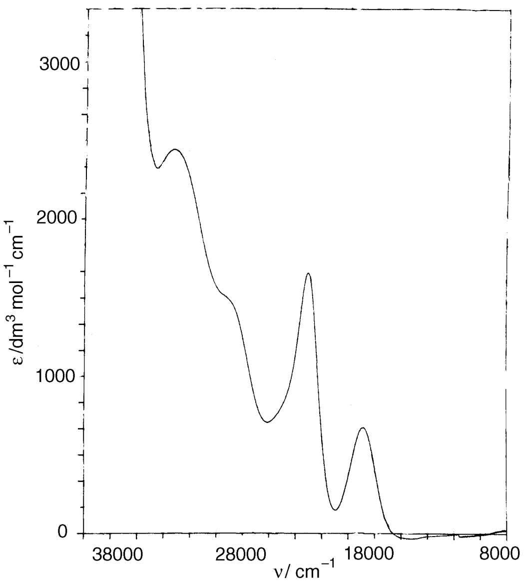

Fig. 3 The UV/VIS absorption spectrum of *mer*-[OsCl$_3$(PEt$_2$Ph)$_3$]- in CH$_2$Cl$_2$ at 290 K

Spectroelectrochemical studies. As a means of validating the above assignments, the spectroelectrochemical behaviour of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)] was investigated. Complete spectroelectrochemical data are quoted in Table 2.

Infrared spectra of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)] and its monoanion were recorded in CH$_2$Cl$_2$ and show a significant shift to lower energy of the CN stretching modes of tcva, from 2225, 2220 and 2185 cm^{-1} to 2180, 2140 and 2105 cm^{-1} respectively. The CN stretching vibrations of free tcne and tcne$^-$ in CH$_2$Cl$_2$, were observed at 2260 and 2215, and at 2180 and 2140 cm^{-1} respectively. Clearly, there is a significant weakening in the CN bonds on reduction of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)].

In addition, EPR spectroelectrochemical studies were also conducted, *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)] and its first oxidation product gave no observable signal down to 77 K. The frozen-glass spectrum of *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]$^-$, in MeCN, gave a single line signal where $g = 2.010$ and the peak width = 23 G. This result is consistent with the unpaired electron being localised on tcva. Attempts to resolve coupling to the ^{14}N nuclei of tcva were unsuccessful. The lack of an observable EPR response from *trans*-[OsCl$_2$(PEt$_2$Ph)$_3$(tcva)]$^+$ may be due to a multiply degenerate (or nearly degenerate) electronic ground state, resulting in extremely rapid relaxation when the unpaired electron is excited. This behaviour is not inconsistent with the unpaired electron being in an Os-based orbital.

On the basis of the IR and EPR spectroelectrochemical studies, and the voltammetric analysis, it is reasonable to conclude that the complex under study is best described as *trans*-[Os^{II}Cl$_2$(PEt$_2$Ph)$_3$(tcva)^0], which may be oxidised to *trans*-[Os^{III}Cl$_2$(PEt$_2$Ph)$_3$(tcva)^0]$^+$, and reduced to *trans*-[Os^{II}Cl$_2$(PEt$_2$Ph)$_3$(tcva)$^-$].

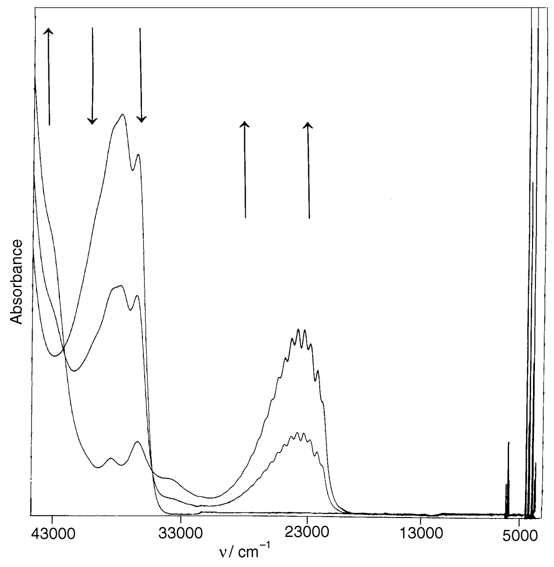

Fig. 4 The UV/VIS spectra showing the reduction of tcne to tcne$^-$ at 233 K in CH_2Cl_2, E_{app} = +0.2 V *vs.* Ag–AgCl

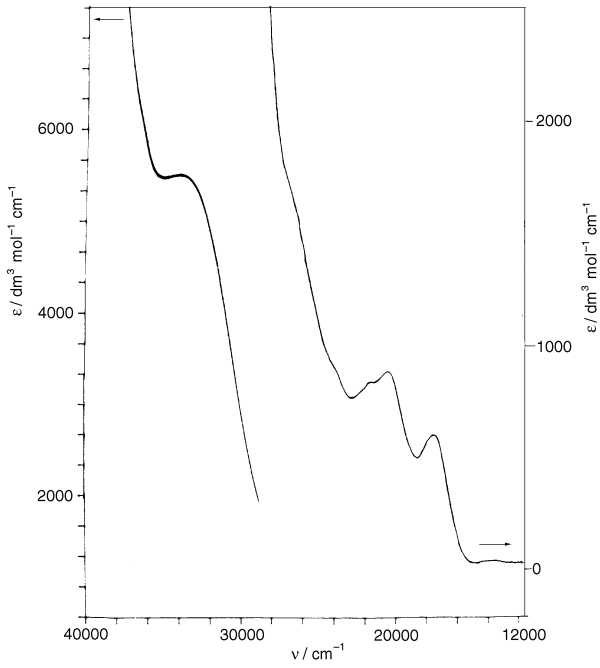

Fig. 5 The UV/VIS absorption spectrum of *trans*-[$OsCl_2(PEt_2Ph)_3$-(tcva)] in CH_2Cl_2 at 260 K

The UV/VIS spectroelectrochemistry of *trans*-[$OsCl_2$-$(PEt_2Ph)_3$(tcva)] was also investigated. The electronic absorption spectrum of *mer*-[$OsCl_3(PEt_2Ph)_3$] in CH_2Cl_2 at room temperature, is shown in Fig. 3. Bands are observed at 18 900 (ε 700 dm^3 mol^{-1} cm^{-1}), 23 100 (1700), 29 500 (sh, 1400), 33 400 (2600) and 39 500 cm^{-1} (13 500). A similar spectrum was reported for *mer*-[$OsCl_3(PBu_2Ph)_3$], in which the highest energy band was assigned to a $Cl^- \longrightarrow Os(e_g{}^*)$ process and the other four were assigned as $Cl^- \longrightarrow Os(t_{2g})$ charge-transfer bands.[29] The assignment of the highest energy band is, however, called into question by the spectra of two related species. In the spectrum of *mer*-[$OsBr_3(PEt_2Ph)_3$] the four lower energy bands have red shifted to 17 300, 19 200, 20 700 and 24 900 cm^{-1}, but the highest energy band of the five was unaffected by the change of halide.[29] This indicates that the highest energy band does not arise from a halide–metal charge-transfer process. Furthermore, in the spectrum of *mer*-[$OsCl_3(PPr^n{}_3)_3$], the four lower energy bands are observed at similar energies to the above trichloro complexes [19 100, 23 900, 26 100 (sh) and 32 700 cm^{-1}] but the fifth band is absent.[29] We therefore assign the band at 38 500 cm^{-1} to an intraligand transition within the phenyl group of the dialkylaryl phosphine, and not to a ligand-metal charge transfer (l.m.c.t.) process.

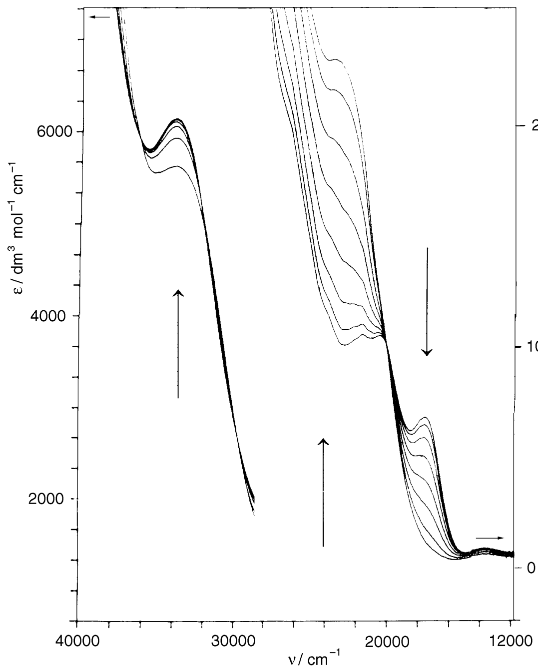

Fig. 6 The UV/VIS spectra showing reduction of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] to *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]$^-$ in CH_2Cl_2 at 260 K, E_{app} = −0.1 V

The electronic absorption spectrum of tcva has not been reported, but it is reasonable to expect that there will be similarities to the spectrum of tcne. Reduction of tcne to the tcne$^-$ radical anion was conducted within the optically transparent electrode cell at 233 K, in CH_2Cl_2. Upon reduction (shown in Fig. 4) the $\pi \longrightarrow \pi^*$ band at 39 000 cm^{-1} moves to 23 000 cm^{-1}. Vibrational fine structure may be observed in the spectra of both neutral and monoanionic tcne. These observations are consistent with previously published results.[30] Note that on completion of the spectroelectrochemical experiment the reduction was reversed and the spectrum of the starting material was fully restored. This confirms that the chemical integrity of the solution remains intact throughout the experiment.

The spectrum of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] in CH_2Cl_2 at 260 K, is shown in Fig. 5. Maxima were found at 17 400 (ε 600 dm^3 mol^{-1} cm^{-1}), 20 400 (900), 32 500 (5500) and 39 000 cm^{-1} (14 200). The two lower energy bands were found to exhibit significant solvatochromism: in thf, for example, they are found at 18 100 and 20 900 cm^{-1}. Such solvent dependence indicates that the transitions associated with the lower energy bands have a significant charge-transfer component. Conversely, the positions of the two highest energy bands are unaffected by changes of solvent.

The band at 39 000 cm^{-1} was again assigned to an intraligand transition on the phosphine ligand. Given the results of the IR and EPR spectroelectrochemical studies, one would predict the presence of $Os^{II} \longrightarrow$ tcva metal-ligand charge-transfer (m.l.c.t.) transitions at fairly low energy, the bands at 17 400 and 20 400 cm^{-1} were therefore assigned to such m.l.c.t. processes. In light of its solvent independence, the band at 32 500 cm^{-1} was also assigned to an intraligand transition, presumably tcva-based.

Reduction of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] in CH_2Cl_2 at 260 K, is shown in Fig. 6. Collapse of the lowest energy band was observed, while a new band appeared at 24 000 cm^{-1}. Changes in the UV range of the spectrum were relatively minor. Several isosbestic points were observed, indicating a clean electron-

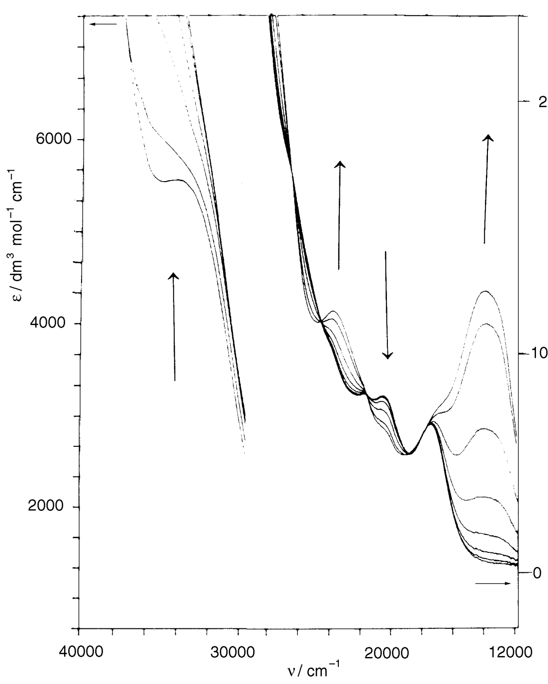

Fig. 7 The UV/VIS spectra showing oxidation of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] to *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]$^+$ in CH_2Cl_2 at 260 K, $E_{app} = +1.8$ V

transfer reaction. We assign the band at 24 000 cm^{-1} to an intraligand transition of tcva$^-$, by analogy with the spectrum of tcne$^-$.

Oxidation of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] also appears to be a one-step process, readily reversible at 260 K. Isosbestic points are again observed, this oxidation is shown in Fig. 7. The spectrum of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)]$^+$ is found to contain maxima at 13 900 (ε 1300 dm^3 mol^{-1} cm^{-1}), 23 700 (1200) and 36 000 (14 000). The highest energy band was assigned to an intraligand $\pi \longrightarrow \pi^*$ transition on the phosphine ligand. The band at 13 900 cm^{-1} was assigned to a tcva $\longrightarrow$ Os^{III} charge-transfer process, while that at 23 700 cm^{-1} has been assigned as a Cl$^-$ $\longrightarrow$ Os^{III} l.m.c.t. band.

Conclusion

To conclude, we have reported the synthesis and characterisation of an osmium complex featuring a novel, redox-active ligand. Structural, electrochemical and spectroelectrochemical investigations indicate that the highest occupied molecular orbital (HOMO) is metal-based, while the LUMO is ligand-based. We formulate the neutral species as *trans*-[$Os^{II}Cl_2(PEt_2Ph)_3$(tcva)^0], its oxidation product as *trans*-[$Os^{III}Cl_2(PEt_2Ph)_3$(tcva)^0]$^+$, and the reduced complex as *trans*-[$Os^{II}Cl_2(PEt_2Ph)_3$(tcva)$^-$]$^-$.

Preliminary mechanistic studies lead us to believe that the substitution reaction which yields tricyanovinyl alcohol is the result of small amounts of water present in thf. It is, for example, possible to induce formation of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] in CH_2Cl_2 by the simple expedient of adding a small amount of water to the reaction mixture, either before or after formation of the blue-grey intermediate. Replacement of CN by OH is only observed *cis* to the Os-bound nitrogen, strongly suggesting that substitution occurs after co-ordination of tcne to osmium. Furthermore, our current data on the blue-grey intermediate [IR (KBr) 2215 (sh), 2205 (sh), 2195m cm^{-1}, no OH stretch; UV/VIS (CH_2Cl_2) 13 800 (1400), 39 000 cm^{-1} (14 000 dm^3 mol^{-1} cm^{-1}); reversible oxidation at +1.52 V and reversible reduction at −0.19 V *vs.* Ag–AgCl] suggest that it is *trans*-[$OsCl_2(PEt_2Ph)_3$(tcne)].

Unanswered questions remain, however, regarding the mechanism by which *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] is formed. The identity of the blue-grey intermediate requires confirmation and the product formulation indicates that the metal centre has been reduced. In the original preparation, $AgBF_4$ was added as a chloride abstractor. However, experiments using $TlBF_4$ give no reaction, whereas bulk electrochemical reduction of the starting materials in a coulometric cell, in CH_2Cl_2, gives the unstable blue-grey intermediate noted previously. We therefore conclude that $AgBF_4$ is more intimately involved in the reaction than as a simple chloride abstractor. Mechanistic studies are currently being undertaken. The formation of *trans*-[$OsCl_2(PEt_2Ph)_3$(tcva)] also suggests the possibility of conducting reactions of Os-bound tcne with other nucleophiles.

Acknowledgements

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References

1 W. Kaim and M. Moscherosch, *Coord. Chem. Rev.*, 1994, **129**, 157.
2 D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, 1987, **109**, 3656.
3 J. S. Miller, J. C. Calabrese, S. R. Chittapeddi, J. H. Zhang, W. H. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769.
4 J. S. Miller, D. M. O'Hare, A. Chakraborty and A. J. Epstein, *J. Am. Chem. Soc.*, 1989, **111**, 7853; W. E. Broderick, J. A. Thompson, E. P. Day and B. M. Hoffmann, *Science*, 1990, **249**, 401; K.-M. Chi, J. C. Calabrese, W. M. Reiff and J. S. Miller, *Organometallics*, 1991, **10**, 688; G. A. Gandela, J. S. Miller and M. J. Rice, *J. Am. Chem. Soc.*, 1979, **101**, 2755.
5 P. Kathirgamanathan and D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun.*, 1980, 839; H. Kitagawa, T. Mitani, J. Toyoda, K. Nakasuji, H. Okamoto and M. Yamashita, *Synth. Met.*, 1993, **56**, 1783; V. J. Murphy and D. O'Hare, *Inorg. Chem.*, 1994, **33**, 787; P. Zhou, J. S. Miller and A. J. Epstein, *Phys. Lett. A*, 1994, **189**, 193.
6 M. Rosenblum, R. W. Fish and C. Bennet, *J. Am. Chem. Soc.*, 1964, **86**, 5166.
7 M. D. Ward, P. J. Fagan, J. C. Calabrese and D. C. Johnson, *J. Am. Chem. Soc.*, 1989, **111**, 1719; M. D. Ward, *Synth. Met.*, 1988, **27**, B211.
8 J. A. McGinnetty and J. A. Ibers, *J. Chem. Soc., Chem. Commun.*, 1968, 235; G. Mestroni, A. Camus and G. Zassinovich, *J. Organomet. Chem.*, 1974, **65**, 119; O. Gandolfi, B. Giovannitti, M. Ghedini and G. Dolcetti, *J. Organomet. Chem.*, 1976, **129**, 207; T. S. Janik, K. A. Bernard, M. R. Churchill and J. D. Atwood, *J. Organomet. Chem.*, 1987, **323**, 247; M. Bottrill, M. Green, A. G. Orpen, D. R. Saunders and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1989, 511; J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, 1970, **92**, 5333; A. Maissonat, J.-J. Bonnet and R. Poilblanc, *Inorg. Chem.*, 1980, **19**, 3168.
9 M. F. Rettig and R. M. Wing, *Inorg. Chem.*, 1969, **8**, 2685; R. Gross and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 251.
10 A. E. D. McQueen, A. J. Blake, T. A. Stephenson, M. Schröder and L. J. Yellowlees, *J. Chem. Soc., Chem. Commun.*, 1988, 1533; A. E. D. McQueen, Ph.D. Thesis, University of Edinburgh, 1988.
11 H. Oshio, E. Ino, T. Ito and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 889.
12 S. L. Bartley and K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 448.
13 R. Gross-Lannert, W. Kaim and B. Olbrich-Deussner, *Inorg. Chem.*, 1990, **29**, 5046; W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov and E. K. H. Roth, *J. Am. Chem. Soc.*, 1992, **114**, 5693; L. Ballester, M. C. Barral, A. Gutierrez, R. Jiminez-Aparicio, J. M. Martinez-Muyo, M. F. Perpinan, M. A. Monge and C. Ruiz-Valero, *J. Chem. Soc., Chem. Commun.*, 1991, 1396; L. Ballester, M. C. Barral, R. Jimenez-Aparicio and B. Olombrada, *Polyhedron*, 1996, **15**, 218.
14 H. Braunwarth, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1989, **372**, C23; J. P. Cornelissen, J. H. van Diemen, L. R. Groenveld, J. G. Hasnoot, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 1992, **31**, 199; B. Olbrich-Deussner, W. Kaim and R. Gross-Lannert, *Inorg. Chem.*, 1989, **28**, 3113.
15 M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics*, 1985, **4**, 501; K. L. Amos and N. G. Connelly, *J. Organomet. Chem.*, 1980, **194**, C57.
16 M. M. Olmstead, G. Speier and L. Szabo, *J. Chem. Soc., Chem. Commun.*, 1994, 541.

17 J. Chatt, G. J. Leigh and R. L. Richards, *J. Chem. Soc. A*, 1970, 2243; J. Chatt, D. P. Melville and R. L. Richards, *J. Chem. Soc. A*, 1971, 1169; J. Chatt, G. J. Leigh and R. M. Paske, *J. Chem. Soc. A*, 1969, 854; B. Bell, J. Chatt, J. R. Dilworth and G. J. Leigh, *Inorg. Chim. Acta*, 1972, **6**, 635; D. J. Cole-Hamilton and T. A. Stephenson, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 2396; G. J. Leigh, J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1969, 705.

18 V. T. Coombe, G. A. Heath, T. A. Stephenson, G. A. Whitelock and L. J. Yellowlees, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 947; V. T. Coombe, Ph.D. Thesis, University of Edinburgh, 1985.

19 S. A. Macgregor, E. McInnes, R. J. Sorbie and L. J. Yellowlees, *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*, eds. A. J. L. Pombeiro and J. A. McCleverty, Kluwer Academic Publishers, Dordrecht, 1993, p. 503.

20 J. Chatt. G. J. Leigh, D. M. P. Mingos and R. M. Paske, *J. Chem. Soc. A*, 1968, 2636.

21 A. C. T. North, D. C. Phillips and D. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

22 G. M. Sheldrick, SHELX 76, a program for crystal structure determination and refinement, University of Cambridge, 1976.

23 D. T. Cromer and J. L. Mann, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 321.

24 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.

25 J. J. Hinkel and J. P. Devlin, *J. Phys. Chem.*, 1973, **58**, 4750.

26 R. G. Little, D. Pautler and P. Coppens, *Acta Crystallogr.*, *Sect. B*, 1969, **27**, 1493.

27 B. W. Sullivan and B. M. Foxman, *Organometallics*, 1983, **2**, 187; T. Dahl, *Acta Chem. Scand.*, *Ser. A*, 1983, **37**, 353.

28 R. J. Sorbie, Ph.D. Thesis, University of Edinburgh, 1989.

29 G. J. Leigh and D. M. P. Mingos, *J. Chem. Soc. A*, 1970, 587.

30 D. L. Jeanmaire, M. R. Suchanski and R. P. Van Duyne, *J. Am. Chem. Soc.*, 1975, **97**, 1699.

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