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Synthesis and structures of photodecarbonylated ruthenium(II) complexes—potential intermediates for mixed ligand complexes

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Irradiation of solutions containing complexes of the type [RuL$(CO)_2Cl_2$] where L is a 2,2′-bipyridine analogue leads to monodecarbonylation and the formation of dimeric ruthenium(II) complexes, [RuL$(CO)_2Cl]_2$, for which two different structures have been established, *viz.* with a *trans* disposition of bridging and terminal chlorides [L = di(2-pyridyl) ketone] or with CO *trans* to bridging chlorides (L = 1,10-phenanthroline).

Ruthenium(II) complexes of 2,2′-bipyridine and 2,2′-bipyridine analogues have attracted much attention, originally as photoredox catalysts for water splitting[1] and as sensitisers for photovoltaic cells.[2] The photoluminescent and redox properties of polynuclear ruthenium complexes containing analogous ligands[3] have also been the subject of intense study. Additionally, complexes with mixed bipyridine and carbonyl ligands have been investigated as catalysts for the reduction of carbon dioxide.[3,4] Although redox and hence catalytic activity depend on the ligands,[5–8] few strategies are available which enable the controlled sequential addition of three different bidentate ligands to ruthenium and only one general route to $[RuL(L')L'']^{2+}$ complexes (where L, L′ and L″ are inequivalent bidentate diimines) exists.[7] Irradiation of ruthenium(II) carbonyl complexes with visible or UV light has long been known to result in decarbonylation. For example, photodecarbonylation of ruthenium(II) carbonyl porphyrin complexes in various substitution reactions has been investigated extensively.[9,10] In contrast, the photodecarbonylation of [RuL$(CO)_2Cl_2$] complexes, where L = bipyridine or related diimine, as a synthetic route to mixed ligand complexes has been largely overlooked except for a recent application to Ru(II) terpyridine complexes.[11] We report the application of photodecarbonylation in the synthesis of complexes of the form [RuL$(CO)Cl_2]_2$. These complexes are ideal precursors to monocarbonylruthenium(II) complexes containing dissimilar bidentate ligands, $[RuL(L')(CO)Cl]^+$.[12]

Irradiation of [RuL$(CO)_2Cl_2]_n$ complexes, formed by reaction of polymeric $[Ru(CO)_2Cl_2]_n$ with appropriate bidentate ligands,[7] in poorly coordinating solvents results in photo-mono-decarbonylation and the subsequent formation of low solubility monocarbonyl complexes [eqn. (1), L = di(2-pyridyl) ketone

$$2\,[Ru(L)(CO)_2Cl_2] \xrightarrow{h\nu} [Ru(L)(CO)Cl_2]_2 + 2\,CO \quad (1)$$

(dpk), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 1,10-phenanthroline (phen)].

Single ν(CO) and terminal ν(Ru–Cl) stretching frequencies indicate symmetric structures. The correspondence in ν(CO) for most complexes (*ca.* 1945 cm^{-1} for bpy, Me_2bpy and phen) is suggestive of similar structures. For the dpk complex, a different structure is indicated by a ν(CO) frequency of 1985 cm^{-1}. The lowering of ν(CO) from 1990–2010 and 2050–2060 cm^{-1} for the [RuL$(CO)_2Cl_2$] precursors reflects an increased bond order between the carbonyl and metal centre and thus a diminished likelihood of further decarbonylation. Hence, long term storage presents no problems enhancing their values as synthetic precursors.

Deposition of [RuL$(CO)Cl_2]_2$ from reaction mixtures in CH_2Cl_2 generally gave powders. However, the phen complex precipitated as small orange moderate quality crystals, whilst well formed red single crystals were obtained for dpk. The X-ray structures† revealed two different, dichloro-bridged, centrosymmetric dimers [Fig. 1(a), (b)]. In each case, the Ru atoms and bridging Cl are coplanar, and each Ru has distorted octahedral stereochemistry. In [Ru(phen)$(CO)Cl_2]_2$ the carbonyls are *trans* to the bridging Cl and the terminal Cl *trans* to pyridyl nitrogens, whilst in [Ru(dpk)$(CO)Cl_2]_2$ the terminal and bridging Cl are mutually *trans*, and the carbonyls are *trans* to the pyridyls.

The Ru · · · Ru separation in [Ru(phen)$(CO)Cl_2]_2$ [3.67(1) Å] is slightly shorter than the value in [Ru(dpk)$(CO)Cl_2]_2$ [3.5644(5) Å]. The latter is shorter than the 3.741 Å separation reported for a supported di-μ-chloride complex $[Ru_3(S_2CNEt_2)_4(CO)_3Cl_2]$.[13] The angle subtended by the dpk ligand, N–Ru–N angle 86.7(1)° compares well with that subtended by dpk in other related Ru(II) dpk complexes; 86.6(2)° in $[Ru(bpy)(dpk)(CO)Cl]^+$ and 87.4(3)° in $[Ru(dpk)(Me_2phen)(CO)Cl]^+$.[12] By forming a six-membered chelate ring dpk allows the Ru(II) center to achieve a geometry that is closer to octahedral than is possible for diimines which form five-membered chelates with more acute N–Ru–N angles {*e.g.* 79.4(4)° in [Ru(phen)$(CO)Cl_2]_2$}. The Ru–C distance of 1.856(4) Å matches those found in other monocarbonyl Ru(II) complexes {*e.g.* 1.86(3) Å for $[Ru(bpy)_2(CO)Cl]^+$}.[14] The pyridyl entities of the dpk ligands have undergone significant distortion from coplanarity in order to conform to a configuration more conducive to the requirements of an octahedral Ru geometry. The interplanar dihedral angle between the pair of C_5N planes is 44.8(2)°, the ruthenium deviations from the two planes being 0.225(6), 0.289(7) Å. Consequently, the behaviour of dpk is not typical of the bipyridine analogue ligands investigated. While substituted bipyridines are unable to complex in a similar manner to dpk owing to geometric restriction caused by the smaller chelate ring size, potential conformations in phen and its derivatives are also limited by a greater structural rigidity. The smaller N–Ru–N angle in the case of [Ru(phen)$(CO)Cl_2]_2$ provides evidence for this. The contrast in coordination geometries of dpk, *cf.* the other diimine ligands, may account for structural differences in [RuL$(CO)Cl_2]_2$, and hence the variance in ν(CO) frequencies. Given the distinctions between the two structurally characterised isomers, the greater π-bonding capacity of pyridyl rings (L = dpk) over bridging chlorides (L = phen) *trans* to the carbonyls accounts for the higher ν(CO) frequency for L = dpk. Since the ν(CO) frequencies of the other diimine complexes examined are similar to that of [Ru(phen)$(CO)Cl_2]_2$ it is likely that they are also dimeric with CO *trans* to the chloride bridge.

The progress of the decarbonylation of *trans*-[Ru(dpk)$(CO)_2Cl_2$] was examined by ^{1}H NMR and IR spectroscopy.

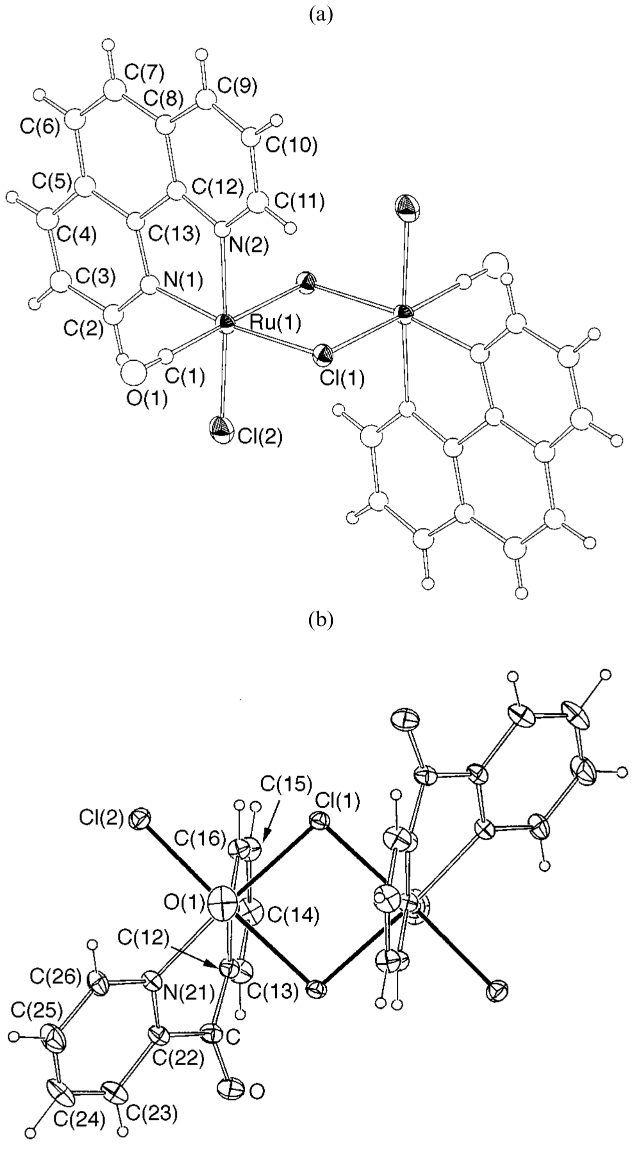

Fig. 1 (a) The centrosymmetric dimer $[Ru(phen)(CO)Cl_2]_2$; 25% thermal envelopes are shown, atoms refined with anisotropic thermal parameters being shaded and hydrogen atoms having arbitrary radii of 0.1 Å. Selected distances (Å) and angles (°): Ru–Cl(1) 2.422(4), Ru–Cl(2) 2.402(1), Ru–C(1) 1.94(1), Ru–N(1) 2.05(1), Ru–N(2) 2.068(10), Ru–Cl(1′) 2.489(3); Cl(1)–Ru–Cl(2) 90.8(1), Cl(1)–Ru–C(1) 83.4(1), Cl(1)–Ru–N(1) 171.8(3), Cl(1)–Ru–N(2) 94.7(3), Cl(1)–Ru–Cl(1′) 83.4(1), Cl(2)–Ru–C(1) 89.0(3), Cl(2)–Ru–N(1) 94.9(3), Cl(2)–Ru–N(2) 174.3(3), Cl(2)–Ru–Cl(1′) 91.4(1), C(1)–Ru–N(1) 91.9(5), C(1)–Ru–N(2) 92.1(4), C(1)–Ru–Cl(1) 177.4(4), N(1)–Ru–N(2) 79.4(4), N(1)–Ru–Cl(1′) 90.6(3), N(2)–Ru–Cl(1′) 87.7(3), Ru–Cl(1)–Ru′ 96.6(1). (b) $[Ru(dpk)(CO)Cl_2]_2$, projected normal to the $Ru(\mu–Cl)_2Ru$ plane; 20% thermal ellipsoids are shown for non–hydrogen atoms. Selected distances (Å) and angles (°): Ru–Cl(1) 2.429(1), Ru–Cl(2) 2.376(1), Ru–C(1) 1.856(4), Ru–N(11) 2.129(3), Ru–N(21) 2.038(3), Ru–Cl(1′) 2.410(1); Cl(1)–Ru–Cl(2) 92.88(4), Cl(1)–Ru–C(1) 90.6(1), Cl(1)–Ru–N(11) 89.50(9), Cl(1)–Ru–N(21) 174.6(1), Cl(1)–Ru–Cl(1′) 85.11(4), Cl(2)–Ru–C(1) 92.2(2), Cl(2)–Ru–N(11) 88.6(1), Cl(2)–Ru–N(21) 90.8(1), Cl(2)–Ru–Cl(1′) 175.77(6), C(1)–Ru–N(11) 179.1(2), C(1)–Ru–N(21) 93.2(2), C(1)–Ru–Cl(1) 91.5(2), N(11)–Ru–N(21) 86.7(1), N(11)–Ru–Cl(1′) 87.6(1), N(21)–Ru–Cl(1′) 91.0(1), Ru–Cl(1)–Ru′ 94.89(4).

IR spectra of $[Ru(dpk)(CO)_2Cl_2]$ recorded in near saturated dichloromethane solution after various irradiation times show the attrition of ν(CO) frequencies at 2072 and 2013 cm^{-1} (*cf.* Nujol mull 2059, 1992 cm^{-1}) coupled with the appearance and intensification of a single peak at 1980 cm^{-1}. The ^1H NMR spectrum of a near saturated solution of $[Ru(dpk)(CO)_2Cl_2]$ in $CDCl_3$ showed only four resonances at δ 9.25, 8.25, 8.17 and 7.73 relative to $SiMe_4$, consistent with the expected C_2 symmetrical *cis*-$(CO)_2$ *trans*-Cl_2 arrangement. After 15 min irradiation with a xenon arc lamp, eight new resonances having a similar integration to the reactant signals were observed and corresponded to those observed for a solution obtained by partial dissolution of $[Ru(dpk)(CO)Cl_2]_2$ in $CDCl_3$. Although consistent with the formation of the dimer, assignment to a chloroform solvate or a five-coordinate intermediate is more likely given the insoluble nature of the final product. In such a chloroform complex, the *trans* orientation of the chloro ligands must be preserved, as the stereochemistry of a *cis*-chloride complex should give rise to a greater number of signals. Photoisomerism is also unlikely due to the necessity of maintaining the *trans*-chloride configuration. This is not the case in the photodecarbonylation of *trans*-chloride $[Ru(phen)(CO)_2Cl_2]$, for which the stereochemistry of the product necessitates isomerisation.

Subsequent work has shown that regardless of their structure, $[RuL(CO)Cl_2]_2$ complexes display similar reactivity towards further substitution by diimine ligands and yield $[RuL(L')(CO)Cl]^+$ (L, L′ = chelating diimines). For example, monodecarbonylated bpy and dpk complexes have been successfully used to prepare new mixed ligand Ru(II) complexes, {*e.g.*, $[Ru(bpy)(Me_2phen)(CO)Cl]^+$, $[Ru(bpy)(dpk)(CO)Cl]^+$ and $[Ru(dpk)(Me_2phen)(CO)Cl]^+$}, which have in turn been used as precursors to tris-heteroleptic complexes.[12] Thus, the photodecarbonylation of $[Ru(L)(CO)_2Cl_2]$ is a key step in a new synthetic route to tris(heteroleptic) ruthenium(II) complexes.

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Notes and references

† Preparation of $[RuL(CO)Cl_2]_n$: in a typical preparation $[Ru(bpy)(CO)_2Cl_2]$[7] (1.00 g, 2.6 mmol) was dissolved in dichloromethane (70 cm^3) and filtered through diatomaceous earth. The filtrate was decanted into a stoppered Pyrex conical flask. The flask was then irradiated with a 50 W halogen lamp at a distance of 15 cm. Irradiation of the stirred solution was sustained for a duration of 48 h after which time an orange precipitate had formed. The precipitate was collected by filtration, washed thoroughly with ethanol and dried at 70 °C; yield (0.85 g, 87%) (Found: C, 36.2; H, 2.2; N, 7.6. $[Ru(bpy)(CO)Cl_2]\cdot 0.25CH_2Cl_2$ requires C, 35.8; H, 2.3; N, 7.4%), ν_{max}/cm^{-1} (CO) 1944s (Nujol). Analogous preparations for L = dpk (Found : C, 32.9; H, 2.0; N, 5.9. $[Ru(dpk)(CO)Cl_2]_2\cdot 2CH_2Cl_2$ requires C, 33.3; H, 2.1; N, 6.0%), ν_{max}/cm^{-1} (CO) 1985s, deposited from reaction mixture as red single crystals. L = 4,4′-Me_2bpy (Found: C, 37.8; H, 3.0; N, 6.6. $[Ru(Me_2bpy)(CO)Cl_2]\cdot CH_2Cl_2$ requires C, 38.0; H, 3.1; N, 6.6%), ν_{max}/cm^{-1} (CO) 1945s. L = phen (Found: C, 40.9; H, 2.3; N, 7.2. $[Ru(phen)(CO)Cl_2]$ requires C, 41.1; H, 2.1; N, 7.4%), ν_{max}/cm^{-1} (CO) 1944s.

‡$[Ru(dpk)(CO)Cl_2]_2$: Data were collected at room temperature on a four-circle/single counter diffractometer. Solution was effected by Patterson methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms in the full matrix least-squares refinement, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Difference map residues were modelled in terms of a pair of dichloromethane solvent molecules, site occupancies set at unity after trial refinement. Neutral atom complex scattering factors were employed, computation using the Xtal 3.4 program system.[15]

Crystal data: $C_{24}H_{16}Cl_4N_4O_4Ru_2\cdot 2CH_2Cl_2$ $M = 938.2$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 9.800(1)$, $b = 12.192(2)$, $c = 14.503(2)$ Å, $\beta = 100.94(1)°$, $U = 1701.4(5)$ Å^3, $T = 295$ K, D_c $(Z = 2) = 1.83$ g cm^{-3}, $2\theta_{max} = 60°$, $2\theta–\theta$ scan mode, $F(000) = 920$, $\mu_{Mo} = 15.5$ cm^{-1} (no correction), Mo-Kα graphite monochromated radiation ($\lambda = 0.71073$ Å), 4556 independent reflections, 3880 observed $[I \geq 3\sigma(I)]$, $R = 0.041$, $R_w = 0.064$ [on $|F|_o$ statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^2(I_{diff})$].

$[Ru(phen)(CO)Cl_2]_2$: a data set collected on a Enraf-Nonius Kappa CCD diffractometer was used in the full matrix least squares refinement after solution of the structure by direct methods. Anisotropic thermal parameters were refined for ruthenium and chlorine, other atoms being refined using isotropic thermal parameters except hydrogens which were constrained at calculated positions. Difference map residues were modelled in terms of dichloromethane solvent molecules, site occupancies set at 0.5. Calculations were performed using Texsan[16] employing neutral atom complex scattering factors.

Crystal data: $C_{22}H_{16}Cl_4N_4O_2Ru_2\cdot 5/2CH_2Cl_2$ $M = 924.7$, monoclinic, space group $C2/c$ (no. 15), $a = 18.153(2)$, $b = 10.544(2)$, $c = 17.092(2)$ Å,

$\beta = 115.66(1)°$, $U = 2948.7(6)$ Å^3, $T = 123$ K, D_c ($Z = 4$) $= 2.01$ g cm^{-3}, $2\theta_{max} = 55°$, 180° φ-scan, $F(000) = 1767$, $\mu_{Mo} = 18.7$ cm^{-1} (no correction), 3395 unique reflections, 1247 observed [$I \geq 3\sigma(I)$], $R = 0.083$, $R_w = 0.069$ on $|F|$. CCDC reference number 186/1273. See http://www.rsc.org/suppdata/dt/1999/275/ for crystallographic files in .cif format.

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