Cationic Carbonyl Complexes of Ruthenium(II) containing 2,2'-Bipyridyl or 1,10-Phenanthroline

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Prolonged reflux of $RuCl_3 \cdot xH_2O$ with stoicheiometric quantities of 2,2'-bipyridyl (bipy) or 2,2':6',2''-terpyridyl (terpy) produces $[RuCl(CO)(bipy)_2]Cl$ and $[RuCl_2(CO)(terpy)]$ respectively. The complexes $[RuCl(CO)(N-N)_2]Cl$ [N–N = bipy or 1,10-phenanthroline (phen)] can also be prepared by carbonylation of $[RuCl_2(N-N)_2]$ in refluxing methanol. Treatment of $[RuCl_2(N-N)_2]$ with $AgSbF_6$ under 3 atm CO affords $[Ru(CO)_2(N-N)_2][SbF_6]_2$. The spectroscopic properties of these compounds are briefly discussed.

ALTHOUGH a very large number of ruthenium carbonyl complexes has been prepared, few which also contain nitrogen heterocycles are known. Amongst mononuclear complexes, the most common are neutral and of general formula $[RuX_2(CO)_x(py)_{4-x}]$ ($x = 1$—3; X = Cl, Br, or I; py = pyridine) [1-6] and $[RuX_2(CO)_2(N-N)_2]$-[N–N = 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) [1,2,6-8]]. These dicarbonyl species are generally prepared [1-3,7] by reaction of $[\{RuX_2(CO)_n\}_m]$ ($n = 2$, $m > 2$; $n = 3$, $m = 2$) with excess of nitrogen donor, although with pyridine $[\{RuX_2(CO)_3\}_2]$ gives [3] a mixture of di- and tri-carbonyl compounds. The dicarbonyls may also be prepared [5,8] by reaction of the 'red solution' obtained [5] by carbonylation of $RuCl_3 \cdot xH_2O$ in refluxing ethanol with excess of heterocyclic base, although aerobic oxidation prior to addition of pyridine gives [5] the ruthenium(III) anionic complex, $[Hpy][RuCl_4(CO)(py)]$. The 'red solution' has also been employed [8] for the synthesis of $[Ru(SnCl_3)_2(CO)_2(py)_2]$, *via* the intermediacy of $[Ru(SnCl_3)_2Cl_2(CO)_2]^{2-}$.

Since pyridine cannot displace CO from $[RuCl_2(CO)_2(py)_2]$, the monocarbonyl species is not a product of these reactions and is best prepared [4] by treatment of $[\{RuCl_2(CO)(C_7H_8)\}_n]$ with excess of pyridine. A similar reaction of $[RuCl_3(CO)(C_7H_8)]^-$ with bipyridyl gives [9] the dimeric $[\{RuCl_2(CO)(bipy)\}_2]$ and anionic $[RuCl_3(CO)(bipy)]^-$. A small amount of a purple product tentatively formulated as $[RuCl(CO)(bipy)_2]Cl$ was also obtained in this reaction but since our work [10] (see below) and that of Kelly and co-workers [11] show this complex to be yellow, the exact nature of the purple product must remain uncertain.

Apart from the report of the ill characterized complex $[RuCl(CO)(bipy)_2]Cl$, referred to above, no cationic ruthenium complexes containing CO and nitrogen heterocycles had been reported prior to the start of this work. More recently, however, Kelly and co-workers [11] have reported the isolation and crystal structure of authentic $[RuCl(CO)(bipy)_2]ClO_4$, prepared by the same method as used by us [10] in a previous study, and Deacon and co-workers [12] have published the synthesis of $[Ru(CO)_2(N-N)_2][SO_3CF_3]_2$† from $[Ru(CO)_2(NCMe)_2(N-N)]^{2+}$.

† *Note added in proof:* The synthesis of $[Ru(CO)_2(bipy)_2][PF_6]_2$ has recently been reported; see J. M. Kelly, C. M. O'Connell, and J. G. Vos, *Inorg. Chim. Acta*, 1982, **64**, L75.

We now report the synthesis of a number of mono- and di-cationic ruthenium complexes of this type.

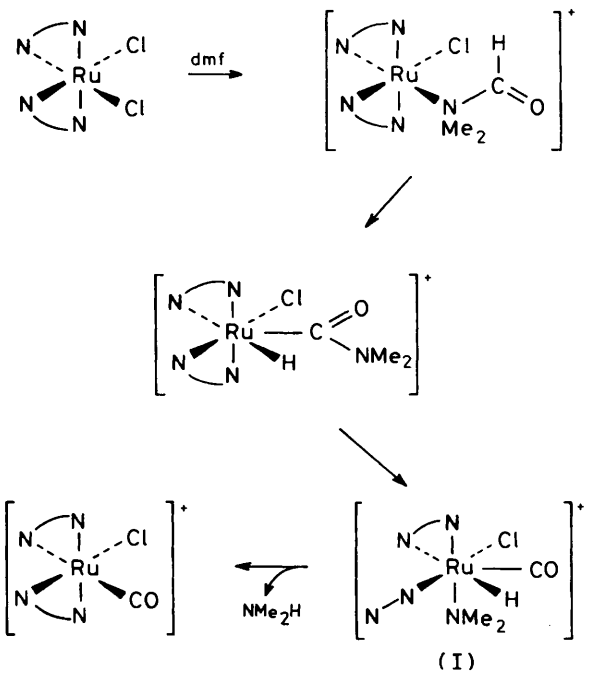
RESULTS AND DISCUSSION

Monocarbonyl Complexes.—During the course of investigations into the substitutional photochemistry of $[Ru(bipy)_3]Cl_2$, we prepared [13] $[RuCl_2(bipy)_2]$ by refluxing $RuCl_3 \cdot xH_2O$ with two mol equivalents of bipyridyl in dimethylformamide (dmf) for 2 h. The product obtained was identical to that obtained by earlier methods, or by photolysis of $[Ru(bipy)_3]Cl_2$ in CH_2Cl_2, except that it showed a broad weak peak in its i.r. spectrum at 1 970 cm^{-1}. Although in our original paper [13] we postulated this might be a hydrido-complex, subsequent study has revealed [10,11] that it is $[RuCl(CO)(bipy)_2]Cl$ and that it may be prepared in higher yield by prolonging the reflux for 7 d, during which time the colour of the solution changes from purple to red-brown. Kelly and co-workers [11] have isolated the same cation as its perchlorate salt by addition of ClO_4 to the reaction solution after removal of $[RuCl_2(bipy)_2]$.

A similar, but neutral complex, $[RuCl_2(CO)(terpy)]$ (terpy = 2,2':6',2''-terpyridyl) can be isolated from $RuCl_3 \cdot xH_2O$ and terpy, but prolonged reflux of $RuCl_3 \cdot xH_2O$ with 1,10-phenanthroline gives only $[RuCl_2(phen)_2]$ contaminated with a small amount of an unidentified orange solid [$\nu(C{\equiv}O)$ at 1 930 cm^{-1}], which is evidently not $[RuCl(CO)(phen)_2]Cl$ since this has $\nu(C{\equiv}O)$ at 1 967 cm^{-1}.

Although we have not conducted studies as to how CO is abstracted from dmf, the reaction has precedent [14] in the photochemical formation of [Ru(CO)(tpp)(dmf)] from [Ru(tpp)(dmf)$_2$] (tpp = the dianion of 5,10,15,20-tetraphenylporphyrin), and probably involves formation of dimethylamine. A plausible mechanism is shown in the Scheme. The lack of formation of $[RuCl(CO)(phen)_2]Cl$ by a similar reaction may then be attributed to the difficulty of forming an intermediate such as (I). Although unidentate co-ordination for phen is known,[15] its rigidity makes such co-ordination unfavourable.

Although $[RuCl(CO)(phen)_2]Cl$ is not formed by decarbonylation of dmf, both it and $[RuCl(CO)(bipy)_2]Cl$ can readily be prepared by carbonylation of $[RuCl_2(N-N)_2]$ in refluxing methanol. Both complexes are yellow



SCHEME Possible mechanism for decarbonylation of dmf by $[RuCl_2(bipy)_2]$

crystalline materials with conductivities in nitromethane indicating 1 : 1 electrolytes and $[RuCl(CO)(bipy)_2]PF_6$ is formed on metathesis with KPF_6 in methanol. Infrared [ν(O–H) 3 350; δ(O–H) 1 618 cm^{-1}] and analytical data (Table) suggest that $[RuCl(CO)(phen)_2]Cl$ crystallizes as a water solvate.

Dicarbonyl Complexes.—During the course of our studies [10,16] on the use of $[RuCl(CO)(N-N)_2]Cl$ as catalysts for the photochemical water-gas shift reaction, we noted that under 3 atm * of CO in water at 100 °C, $[RuCl(CO)(phen)_2]Cl$, although not the bipy analogue, was partially converted into another species with ν(C≡O) at 2 028 and 2 092 cm^{-1}. We assumed this to be *cis*-$[Ru(CO)_2(phen)_2]Cl_2$, similar to $[Ru(CO)_2(P-P)_2]^{2+}$ [P–P = $Ph_2P(CH_2)_nPPh_2$, n = 1 or 2] which we have recently prepared [17] from $[RuCl_2(P-P)_2]$, $AgSbF_6$, and CO.

* Throughout this paper: 1 atm = 101 325 Pa.

Analogously, we find that $[RuCl_2(N-N)_2]$ (N–N = bipy or phen) react with $AgSbF_6$ under 3 atm of CO to give $[Ru(CO)_2(N-N)_2][SbF_6]_2$ as off-white solids in high yield. The complexes both have two ν(C≡O) bands above 2 000 cm^{-1} and are 2 : 1 electrolytes, consistent with their being *cis* dicarbonyl dications. These cations are presumably the same as those synthesized by Deacon and co-workers,[12] although they provide little spectroscopic data for their compounds. Their direct synthesis from $[RuCl_2(N-N)_2]$, reported here, represents a somewhat simpler method than that employed by Deacon and co-workers.

For $[Ru(CO)_2(phen)_2][SbF_6]_2$ there is sometimes an impurity with ν(C≡O) at 2 050 cm^{-1}. By careful crystallization this compound has been obtained almost pure {contaminated with small amounts of *cis*-$[Ru(CO)_2(phen)_2][SbF_6]_2$} as yellow microcrystals and since this analyses for the same stoicheiometry we believe it to be *trans*-$[Ru(CO)_2(phen)_2][SbF_6]_2$. Related dicarbonyl complexes of molybdenum, $[Mo(CO)_2(N-N)_2L]^{2+}$ (L = H_2O or MeCN), have recently been reported by Connor *et al.*[18]

Spectroscopic Properties.—The amount of positive charge on the ruthenium centre is reflected by ν(C≡O) of the various different complexes. Thus, the neutral $[RuCl_2(CO)(terpy)]$ has ν(C≡O) at 1 925 cm^{-1} suggesting substantial back electron transfer from the metal to the π* orbitals of CO. As the positive charge on the metal is increased, ν(C≡O) shifts to higher frequency (*ca.* 1 970 cm^{-1} for the monocations) until, for the dications, the very low electron density on the metal is reflected by the high value of ν(C≡O) (2 040 and 2 090 cm^{-1}). It is interesting to note that the position of ν(C≡O) for the dicationic species is very similar to that for $[Ru(CO)_2(P-P)_2][SbF_6]_2$,[17] suggesting that the electron densities on the metal, and hence the electron-withdrawing properties of the nitrogen- and phosphorus-donor ligands, are similar.

Comparison of the visible spectrum of $[RuCl(CO)(bipy)_2]Cl$ with those of $[RuClL(bipy)_2]^+$ (L = tertiary phosphine) [19] shows that it is similar but that the lowest-energy band has increased in energy and become broader and lower in intensity. Indeed with our complex this band is not resolved from the band at higher energy and rather appears as a ' hump ' on the broad tail

Analytical and spectroscopic data for ruthenium complexes

Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	I.r. [ν(C≡O)]/ cm^{-1}	$\lambda_{max.}$ [b]/nm	Λ [c]/ S cm^2 mol^{-1}
cis-$[RuCl(CO)(bipy)_2]Cl$	218—220	49.6 (49.2)	3.0 (3.1)	11.3 (11.0)	1 960	410 (1 796) [d] 340 (4 082)	72.9
cis-$[RuCl(CO)(phen)_2]Cl{\cdot}3H_2O$ [e]	228—230	48.4 (48.9)	3.2 (3.5)	8.9 (9.1)	1 967	407 (3 818) [d] 335 (6 890)	67.6
cis-$[RuCl_2(CO)(terpy)]$ [f]	>350 [g]	43.7 (44.4)	2.4 (2.6)	9.7 (9.7)	1 925		
cis-$[RuCl(CO)(bipy)_2]PF_6$	328 [g]	40.4 (40.0)	2.7 (2.6)	8.9 (9.0)	1 968		
cis-$[Ru(CO)_2(bipy)_2][SbF_6]_2$	298—300	28.1 (28.0)	5.9 (6.0)	1.8 (1.7)	2 092, 2 039	480 (130) [h] 390 (220) [d] 330 (1 080)	211.3
cis-$[Ru(CO)_2(phen)_2][SbF_6]_2$	318—320	31.2 (31.5)	5.4 (5.6)	1.8 (1.6)	2 092, 2 028	392 (740) [d,h] 352 (1 870)	199.0

[a] Calculated values are given in parentheses. [b] In water. Values of ε (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] Measured on 10^{-3} mol dm^{-3} solutions in CH_3NO_2. [d] Unresolved from higher energy absorption. [e] Cl 10.75 (11.6)%. [f] Cl 15.7 (16.4)%. [g] Decomposes *ca.* 300 °C. [h] In acetone.

of this peak. This behaviour is as expected since CO is a much better π acceptor than tertiary phosphines. This band has been assigned [19] as a π^*(bipy)$\leftarrow d_\pi$(Ru) transition and it has been argued that this should be broader and higher in energy for better π acceptors since the *d* orbitals of the metal are stabilized by increased π bonding. The spectrum of $[RuCl(CO)(phen)_2]Cl$ is similar although both absorptions are stronger.

The visible absorptions for $[Ru(CO)_2(N\text{-}N)_2][SbF_6]_2$ are all very weak and we do not attempt to assign them.

EXPERIMENTAL

Microanalyses were by the Liverpool University Microanalytical Service. Infrared spectra were recorded of Nujol mulls between caesium iodide plates on a Perkin-Elmer PE577 grating spectrometer, u.v. spectra on a Pye Unicam SP8–100 spectrophotometer, and conductivity measurements were performed using a Phillips PR 9500 conductivity bridge with a Mullard E7591/B conductivity cell. Melting points were measured in air in an Electrothermal melting-point apparatus and are uncorrected.

All solvents were reagent grade and were used without further purification. The complexes $[RuCl_2(phen)_2]$ and $[RuCl_2(bipy)_2]$ were prepared by a literature method.[20]

Bis(2,2′-*bipyridyl*)*carbonylchlororuthenium*(II) *Chloride*.—(*a*) The compounds $RuCl_3 \cdot xH_2O$ (0.54 g) and bipyridyl (0.65 g) were refluxed in dmf (100 cm^3) for 7 d during which time the colour of the solution changed through purple to red-brown. After reduction of the volume to 5 cm^3 *in vacuo*, the solution was allowed to evaporate to dryness in air. The resulting product consisted of large red-brown crystals of the complex contaminated with smaller red crystals identified as $[Ru(bipy)_3]Cl_2$ by their u.v.–visible spectrum. These were separated by crystal picking. Yield *ca.* 40%.

(*b*) As above except that the reaction solution was evaporated to dryness *in vacuo* and the resulting red-brown mass was recrystallized from methanol–diethyl ether (by addition of the second solvent to a solution in the first) to give the complex as yellow plates. These were collected and stored under dry nitrogen on account of their hygroscopic nature. Yield 50%.

(*c*) Carbon monoxide was bubbled through a refluxing solution of $[RuCl_2(bipy)_2]$ (0.62 g) in methanol (50 cm^3) for 48 h. The resulting orange-red solution was evaporated to 15 cm^3 and precipitated with diethyl ether. The pure complex separated as yellow plates on cooling the filtrate to −30 °C. These were collected and dried *in vacuo*. Yield *ca.* 50%.

I.r. max (cm^{-1}): 3 350m (vbr), 1 960vs (br), 1 618m (br), 1 600s, 1 560w (sh), 1 315s, 1 260w, 1 242m, 1 222w (sh), 1 164m (sh), 1 155m, 1 118w, 1 102w, 1 065w, 1 041w (sh), 1 012m, 984w (br), 798m (sh), 764vs, 760vs (sh), 748m (sh), 725s, 643w, 583w (br), 501w, 412w, and 323m.

Carbonylchlorobis(1,10-*phenanthroline*)*ruthenium*(II) *Chloride–Water* (1/3).—This complex was prepared as in (*c*) above from $[RuCl_2(phen)_2]$ (0.5 g) in methanol (50 cm^3). Yield *ca.* 30% after 24 h.

I.r. max. (cm^{-1}): 1 967vs (br), 1 600w, 1 579w, 1 508w, 1 448w (sh), 1 426s, 1 420m (sh), 1 410m (sh), 1 340w, 1 222w, 1 200w, 1 142w, 1 104w (sh), 1 092m (br), 845s, 775w, 720s, 652w (br), 580w, 518w, 329w, and 282w.

Carbonyldichloro(2,2′:6′,2″-*terpyridyl*)*ruthenium*(II).—This complex was prepared as in (*a*) above from $RuCl_3 \cdot xH_2O$ (0.3 g) and terpyridyl (0.26 g) with a reflux time of 24 h. The red crystals which precipitated on cooling were collected, washed with acetone, and dried *in vacuo*. Yield 25%. The compound is sparingly soluble in CH_2Cl_2 but insoluble in most other common organic solvents.

I.r. max. (cm^{-1}): 1 925s (vbr), 1 590m, 1 305m, 1 289w, 1 248w (sh), 1 232m, 1 210w (sh), 1 180w (sh), 1 168w (sh), 1 155m, 1 132w, 1 088w, 1 045w, 1 018m, 970w, 888w, 820w, 797m (sh), 775vs, 755s (sh), 737s, 727s (sh), 642w, 579m, 513m (br), 462w, 439w, 362w, 320m, 272w, and 255m.

Bis(2,2′-*bipyridyl*)*carbonylchlororuthenium*(II) *Hexafluorophosphate*.—The compound $RuCl_3 \cdot xH_2O$ (0.5 g) was refluxed with bipy (0.61 g) in dmf (40 cm^3) for 7 d. After evaporation to dryness the red-brown tarry solid was dissolved in methanol (15 cm^3) and treated with KPF_6 (0.4 g) in methanol. The resulting yellow solid was collected and recrystallized from acetone and diethyl ether as yellow prisms. Yield *ca.* 60%.

I.r. max. (cm^{-1}): 1 968vs (br), 1 604s, 1 492w, 1 317m, 1 277vw, 1 243m, 1 218vw, 1 175w, 1 160m, 1 119vw, 1 070w, 890m (sh), 876s (sh), 843vs (br), 798m (sh), 770vs (sh), 764vs, 730s, 645w, 597w, 583w (sh), 560w (sh), 555vs, 547w (sh), 500w, 417m, and 330m.

cis-*Bis*(2,2′-*bipyridyl*)*dicarbonylruthenium*(II) *Hexafluoroantimonate*.—The complex $[RuCl_2(bipy)_2]$ (0.38 g) and $AgSbF_6$ (0.6 g) were added to CH_2Cl_2 (50 cm^3) in a glass pressure vessel. The resulting mixture was evacuated and pressurised to 3 atm with CO. After stirring at 80 °C for 16 h, the pale orange-brown solution was filtered to remove silver chloride and evaporated to dryness. The resulting product was recrystallized from acetone–diethyl ether to give off-white microcrystals of the product. A further crop of product was obtained on extraction of the silver chloride with acetone, addition of diethyl ether to incipient crystallization, and standing overnight in a closed vessel. Total yield *ca.* 70%.

I.r. max. (cm^{-1}): 2 029s, 2 039s, 1 602w, 1 495vw (br), 1 317w, 1 244w, 1 166w, 1 110w, 1 071w, 1 035w, 1 020w, 888w (sh), 832m (br), 770m (sh), 762s, 727w, 719w (sh), 667s (sh), 652vs, 642s (sh), 635m (sh), 580w, 552w, 516w, 417vw, 302vs (sh), 282vs, and 277s (sh).

cis-*Dicarbonylbis*(1,10-*phenthroline*)*ruthenium*(II) *Hexafluoroantimonate*.—This complex was similarly prepared from $[RuCl_2(phen)_2]$ (1.64 g) and $AgSbF_6$ (2.32 g) in CH_2Cl_2 (100 cm^3). Yield *ca.* 70%.

I.r. max. (cm^{-1}): 2 092vs, 2 028vs, 1 600vw (br), 1 583vw (br), 1 420w (sh), 1 417w, 1 318vw (br), 1 222w, 1 147w, 845s, 772w, 742w (sh), 723m (sh), 717s, 667s (sh), 651vs, 639s (sh), 636s (sh), 582w, 530w, 426w, 300w (sh), 282vs, 277vs (sh), and 263m (sh).

trans-*Dicarbonylbis*(1,10-*phenanthroline*)*ruthenium*(II) *Hexafluoroantimonate*.—The compounds $[RuCl_2(phen)_2]$ (0.1 g) and $AgSbF_6$ (0.14 g) were added to CH_2Cl_2 (20 cm^3) and pressurised to 3 atm of CO. The resulting suspension was filtered and the filtrate treated with diethyl ether (100 cm^3). The i.r. spectrum of the solid so formed had $\nu(C\equiv O)$ at 2 100, 2 050, 2 030, and 1 980 cm^{-1}. The first product obtained on recrystallization of this solid from acetone–diethyl ether had a strong $\nu(C\equiv O)$ band at 2 050 cm^{-1} and weaker ones at 2 090 and 2 030 cm^{-1}. We tentatively assign this as the complex contaminated with *cis*-$[Ru(CO)_2(phen)_2][SbF_6]_2$. Yield *ca.* 10% (Found: C, 32.2; H, 2.3; N, 5.6. Calc.: C. 31.5; H, 1.6; N, 5.7%).

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