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Isocyanide–Bis(2,2'-bipyridine) Complexes of Ruthenium(II). A New Synthetic Route to Complexes of Ruthenium via the Ion [(bpy)₂Ru(DME)]²⁺

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The characterization of complexes containing ruthenium(II) has acquired particular importance recently because of the redox and photochemical properties of $[Ru(bpy)_3]^{2+}$ and related complexes.[2] As a matter of course, we have prepared a series of complexes of the type cis-$[Ru(bpy)_2X_2]$ and cis-$[Ru(bpy)_2L_2]^{2+}$ and find that the series is remarkable both because a large number of compounds can be prepared and because spectral and redox potential measurements allow the effect on the metal of changes in the cis ligands to be investigated in a systematic way.[3] As part of this study we earlier reported on the properties of diolefin complexes where the effect of the carbon-bound ligands on the metal was significant.[4] This paper continues that theme in describing the preparations and properties of some isocyanide complexes where L = RNC.

It is generally desirable to have versatile precursors for synthetic work of this kind. In the past, cis-$[Ru(bpy)_2Cl_2]$ has been of great value,[5a] and more recently we have described the preparation and synthetic chemistry of solvent-bound complexes like $[Ru(bpy)_2(acetone)Cl]^{+}$ [5b] and cis-$[Ru(bpy)_2(acetone)_2]^{2+}$.[5c] The acetone ligand, while being readily displaced by a variety of reagents, suffers from the disadvantage that it is capable of being attacked by nucleophiles. We have sought other potential leaving groups which, like acetone, might be readily displaced from ruthenium(II) but which would be less reactive themselves toward nucleophiles. This paper describes the preparation and some preliminary investigations of the reactions of cis-$[Ru(bpy)_2(DME)](PF_6)_2$ (DME is $CH_3OCH_2CH_2OCH_3$) in which the bound diether 1,2-dimethoxyethane (DME) has proven to be a useful leaving group.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded by using either Cary Model 14 or Bausch and Lomb Model 210 spectrophotometers. Molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. Proton NMR spectra were determined with a 100-MHz Varian Fourier transform spectrometer with Me_4Si as an internal standard. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials on the assumption that differences in diffusion coefficients for oxidized and reduced species are negligible. The measurements were made by using a PAR Model 173 potentiostat for potential control with a PAR Model 175 Universal Programmer as a sweep generator for voltammetry measurements. All electrochemical measurements were performed at platinum bead working electrodes using MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. ESCA spectra were obtained on solid samples of the complexes with a Du Pont 650 B electron spectrometer. The samples as powders were held in contact with the probe with Permacel PO2 double-sided tape. Infrared spectral measurements were made with a Beckman IR-4250 with the samples mounted in KBr disks. Elemental analyses were performed by Integral Microlabs, Raleigh, N.C.

Materials and Methods. cis-$[Ru(bpy)_2Cl_2]\cdot2H_2O$ and cis-$[Ru(bpy)_2(acetone)_2](ClO_4)_2$ were prepared by methods already described.[5]

Silver(I) hexafluorophosphate was purchased from Alpha Ventron. Isocyanides were prepared from the formamides RNHCHO (R = $PhCH_2$, 4-$MeOC_6H_4$, 4-ClC_6H_4) by dehydration with triphenylphosphine and carbon tetrachloride.[6] 1,2-Dimethoxyethane and acetone were reagent grade and dried and distilled under nitrogen or argon immediately prior to use.

Preparation of cis-$[Ru(bpy)_2(DME)](PF_6)_2$ in Solution. Solid cis-$[Ru(bpy)_2Cl_2]\cdot2H_2O$ (1.29 g, 2.48 mmol) was suspended in freshly distilled, dry 1,2-dimethoxyethane (40 mL) which had been purged with argon. Silver(I) hexafluorophosphate (1.25 g, 4.94 mmol) was added portionwise to the stirred suspension under a current of argon. A deep wine red color developed immediately in the solution. The mixture was stirred for ca. 0.5 h and then filtered under gravity through a coarse or medium frit under argon. The solid was washed with 1,2-dimethoxyethane (5 × 2 mL). The solution of cis-$[Ru(bpy)_2(DME)](PF_6)_2$ was stored under argon. Evidence favoring the ion in solution as being the DME complex came from a gravimetric experiment where the AgCl from the reaction was collected and weighed and the weight obtained (0.71 g) agreed well with that predicted (0.708 g) on the basis of the initial weight of Ru(bpy)₂Cl₂·2H₂O.

Preparation of cis-$[Ru(bpy)_2(CNCH_2Ph)_2](PF_6)_2$. Benzyl isocyanide (0.45 g, 3.85 mmol) was added dropwise to a dimethoxyethane solution containing cis-$[Ru(bpy)_2(DME)](PF_6)_2$ which had been prepared in the manner just described from cis-$[Ru(bpy)_2Cl_2]\cdot2H_2O$ (0.90 g, 1.73 mmol). The mixture was stirred at room temperature for 1 h and then heated at reflux for 0.5 h. The color of the mixture deepened to brown. Solvent was removed by distillation under reduced pressure. The residual solid was taken up in a small volume of acetonitrile and chromatographed on alumina. A single orange band was eluted with acetonitrile/toluene (1:1). The solvent was removed by distillation and the solid residue crystallized at −10 °C from acetonitrile/ether. Recrystallization from acetonitrile/ether (1:2) gave pale yellow crystals of cis-$[Ru(bpy)_2(CNCH_2Ph)_2](PF_6)_2$ (1.3 g, 1.38 mmol; 80% yield). Anal. Calcd for $C_{36}H_{30}F_{12}N_6P_2Ru$ (M_r = 937.67): C, 46.1; H, 3.3; N, 9.0; P, 6.6; Ru, 10.8. Found: C, 45.9; H, 3.5; N, 8.7; P, 6.7; Ru, 10.4.

Preparation of cis-$[Ru(bpy)_2(CNC_6H_4OMe-4)_2](ClO_4)_2$. 4-$MeOC_6H_4NC$ (0.3 g, 2.25 mmol) in pentane solution (5 mL) was added to an acetone solution of cis-$[Ru(bpy)_2(acetone)_2](ClO_4)_2$ which had been freshly prepared[5] from cis-$[Ru(bpy)_2Cl_2]\cdot2H_2O$ (0.5 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h and then heated at reflux for 1 h. The color of the mixture deepened to brown. Elaboration of the mixture in the manner already described gave yellow crystals of cis-$[Ru(bpy)_2(CNC_6H_4OMe-4)_2](ClO_4)_2$ (0.64 g, 0.73 mmol; 73% yield). Anal. Calcd for $C_{36}H_{30}Cl_2N_6O_{10}Ru$ (M_r = 878.70): C, 49.2; H, 3.4; N, 9.6; Ru, 11.5. Found: C, 49.2; H, 3.5; N, 9.4; Ru, 11.8.

Survey Reactions of cis-$[Ru(bpy)_2(DME)](PF_6)_2$. To characterize the general reactivity of the DME complex, we added an excess of the appropriate ligand to an approximately 10^{-4} M solution of the complex dissolved in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), or 20% H_2O–80% THF mixtures (by volume). The latter medium is referred to later as aqueous THF. The reactions were monitored spectrophotometrically by following the growth and disappearance of characteristic $\pi^*(bpy) \leftarrow d\pi(Ru)$ absorption bands in the visible region. In some cases it was necessary to warm the solutions slightly in order to drive the reactions to completion.

Results and Discussion

Some 50 isocyanide compounds of ruthenium(II) have been reported. The complexes belong to the following general types, in which L = RNC: $[RuL_6]^{2+}$, $[RuL_5(carbene)]^{2+}$,[7] $[RuL_4(carbene)_2]^{2+}$,[7] $[RuL_4X_2]$,[8] cis-$[RuL_2(carbene)_4]^{2+}$,[7] cis- and trans-$[RuL_2X_2(PR_3)_2]$[9] and various monoisocyanide complexes $[RuH_2L(PR_3)_3]$,[10] $[RuHXL(PR_3)_2(CO)]$,[11] and derivatives of these such as $[RuO_2L(CO)(PR_3)_2]$[12] and $[Ru(CS_2)L(CO)(PR_3)_2]$.[13] Although something is known about the chemical reactivity of these complexes toward amines, remarkably little attention has been paid to characterizing the nature of the (Ru–CNR) bond.

The complexes cis-$[Ru(bpy)L_2]^{2+}$ described here are all yellow, air-stable solids as PF_6^- or ClO_4^- salts. The salts crystallize with difficulty from acetonitrile/ether mixtures. They decompose at temperatures above ca. 240 °C releasing

Table I. Infrared Spectra (cm^{-1}) of *cis*-$[Ru(bpy)_2(CNR)_2]^{2+}$ Ions in the Region 2200–2000 cm^{-1}

CHR	$\nu(C \equiv N)$ (KBr disk)	$\nu(C \equiv N)$, av	$\Delta\nu^a$
$CNCH_2Ph$	2193, 2153	2173	+27
CNC_6H_4OMe-4	2180, 2160; 2142, 2125	2152	+24
CNC_6H_4Cl-4	2170, 2150, 2142, 2118	2145	+15

a $\Delta\nu = \nu(CN)(complex) - \nu(CN)(free\ ligand)$.

Table II. UV/Visible Absorption Maxima $(\lambda_{max}\ (nm),\ \log\epsilon)$ for the Isocyanide Complexes in Acetonitrile Solution

CNR	λ_{max}	$\log\epsilon$	λ_{max}	$\log\epsilon$	λ_{max}	$\log\epsilon$	λ_{max}	$\log\epsilon$
$CNCH_2Ph$	356	3.53	313	4.92	303	4.86	266	5.14
CNC_6H_4OMe-4	347	3.73	314	4.94	300	4.91	271	5.34
CNC_6H_4Cl-4	331	3.69	313	4.92	302	4.87	275	5.21

the isocyanide ligand (detected by its odor) and leaving a green-black solid. The complexes are soluble in acetonitrile, acetone, and nitromethane.

The infrared spectra of the complexes in solution show two intense absorptions in the region 2200–2000 cm^{-1} assigned to $\nu(C \equiv N)$, indicating the relative cis stereochemistry of the isocyanide ligands. In the solid state (Table I) both absorptions are split by ca. 20 cm^{-1} in the case of the aryl isocyanide complexes. The splittings most probably arise as a consequence of differences in site symmetry in the solid state. The shift in $\nu(C \equiv N)$ on binding, $\Delta\nu(C \equiv N)$ [defined as $\nu(C \equiv N)$-(complex) $- \nu(CN)$(free ligand)] is positive in each case. The magnitude of the shift (ca. 15–27 cm^{-1}) is less than that[7,9] in $[Ru(CNMe)_6]^{2+}$ ($\Delta\nu = 95\ cm^{-1}$) but greater than that in $[RuCl_2(CNC_6H_4OMe-4)_2(PMe_2Ph)_2]$ ($\Delta\nu = -28\ cm^{-1}$).[9]

The ultraviolet absorption spectra of the complexes are characterized by four bands with $\lambda_{max} > 250$ nm (Table II). The energy of the lowest energy band increases as the electron-acceptor character of the ligand increases: (aryl)NC > (alkyl)NC; 4-ClC_6H_4NC > 4-$MeOC_6H_4NC$. The bands no doubt arise from π^*(bpy) $\leftarrow d\pi(Ru(II))$ transitions which are significantly blue shifted compared to related complexes of Ru(II). Ligand-localized, $\pi^* \leftarrow \pi$(bpy) transitions are usually observed at ~290 nm for ruthenium(II) complexes (e.g., 292 nm in $[Ru(bpy)_2(pyr)Cl]^+$, pyr is pyrazine[14]). In the isocyanide complexes the transition is red shifted and split into two components which appear at 303 and 313 nm. The same kinds of changes in the $\pi^* \leftarrow \pi$ transition are also found upon oxidation of Ru(II) to Ru(III) (e.g.,[14] λ_{max} 300, 312 nm in $[Ru^{III}(bpy)_2(pyr)Cl]^{2+}$). The spectral observations are consistent with the isocyanide ligands functioning as strong electron acceptors with respect to the $[(bpy)_2Ru^{II}<]$ group and they suggest that the extent of electron flow from Ru(II) into the ligands may be extensive.[3,15]

Further support for this view is provided by electrochemical measurements. In acetonitrile solution the values of $E_{1/2}$ (vs. the SSCE) for the couples $[Ru(bpy)_2(CNCH_2Ph)_2]^{3+/2+}$ and $[Ru(bpy)_2(CNC_6H_4OMe-4)_2]^{3+/2+}$ are at +1.90 and +1.98 V. The $E_{1/2}$ values are compared with values for related couples in Table III. The data extend and reinforce the correlation found earlier[3] between the energies of π^*(bpy) $\leftarrow d\pi$(Ru) charge-transfer bands and reduction potentials for $[Ru(bpy)_2L_2]^{3+/2+}$ couples. To put the magnitude of the reduction potentials for the isocyanide couples in perspective, they occur in the same potential range as found for the Ru(IV)/Ru(III) couple $Ru(bpy)_2Cl_2^{3+/2+}$.[3] Measurement of the Ru $3d_{5/2}$ core electron binding energy in *cis*-$[Ru(bpy)_2$-$(CNCH_2Ph)_2](PF_6)_2$ gave a value (281.6 ± 0.3 eV) which is significantly greater than that measured for other neutral or ionic ruthenium(II) complexes, and in fact is halfway between the values found for Ru(II) in $Ru(bpy)_2Cl_2$ and Ru(III) in

Table III. Half-Wave Reduction Potentials, $E_{1/2}(Ru^{III}/Ru^{II})$, and π^*(bpy) $\leftarrow d\pi(Ru)$ Charge-Transfer Band Energies for the Ions *cis*-$[Ru(bpy)_2L_2]^{2+}$ in Acetonitrile Solution

complex	$E_{1/2}$ $(Ru^{III/II})$, V	λ_{max}, nm	footnote
$Ru(bpy)_2(py)_2^{2+}$	1.28	456	a
$Ru(bpy)_3^{2+}$	1.30	452	a
$Ru(bpy)_2(CH_3CN)_2^{2+}$	1.44	425	a
$Ru(bpy)_2(PPh_3)_2^{2+}$	1.54	419	a
$Ru(bpy)_2(C_7H_8)^{2+\ e}$	1.70	421	b
$Ru(bpy)_2$-$(Ph_2PCH=CHPPh_2)^{2+}$	1.74	373	c
$Ru(bpy)_2$-$(CNCH_2Ph)_2^{2+}$	1.90	356	d
$Ru(bpy)_2$-$(CNC_6H_4OMe-4)_2^{2+}$	1.98	347	d

a D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1977. b B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehman, and A. Ludi, *J. Am. Chem. Soc.*, 99, 7368 (1977). This is an E_p value for the chemically irreversible oxidation of the Ru(II) complex to Ru(III). c B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, 17, 3334 (1978). d This work. All measurements in this and previous studies^{a-c} were carried out with 0.1 M $[N(n-C_4H_9)_4]PF_6$ as supporting electrolyte using a Pt-bead working electrode and are vs. the salt saturated calomel (SSCE) electrode at 25 ± 2 °C. e C_7-H_8 is norbornadiene.

Table IV. Ruthenium $3d_{5/2}$ Core Electron Binding Energies, eV (Relative to C 1s 285.0 eV)

compound	BE(Ru $3d_{5/2}$), eV	footnote
cis-$Ru(bpy)_2Cl_2$	280.5	a
cis-$[Ru(bpy)_2(CNC_6H_2Ph)_2](PF_6)_2$	281.6	b
cis-$[Ru(bpy)_2Cl_2]Cl$	282.5	a

a T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray, and D. Unterreker, *J. Am. Chem. Soc.*, 97, 3039 (1975). b This work, measured on double-sided Scotch tape.

$[Ru(bpy)_2Cl_2]Cl$ (Table IV).

The ^1H NMR spectrum of $[Ru(bpy)_2(CNCH_2Ph)_2](PF_6)_2$ in CD_3CN solution provides support for the suggested cis stereochemistry. The complex signal associated with the bpy protons (16 H) is centered at about δ 8.0 ppm (range δ 7.7–8.3 ppm). The protons of the phenyl groups (10 H) give a resonance centered at δ 7.1 ppm (range 7.0–7.2 ppm). The methylene protons are equivalent and appear as a sharp singlet at δ 4.97 ppm (4 H). The singlet is shifted 0.60 ppm (δ-(PhCH_2NC) = 4.37 in CD_3CN) downfield[16] from the free ligand value. All of the chemical shift data are relative to Me_4Si as internal standard.

When taken together the data reported here lead to the conclusion that isocyanide ligands function as strong π acceptors with respect to the $(bpy)_2Ru^{II}<$ fragment, indeed that they are stronger acceptor ligands than tertiary phosphines.[5c] This is in contrast to the behavior of these ligands with respect to the spin-paired d^6 $(CO)_4Mo<$ fragment. In the complexes *cis*-$[Mo(CO)_4(CNR)_2]$ there is no evidence for a significant role as π acceptors by the isocyanide ligands and the π-acceptor strength of phosphines is greater (as indicated by values of $\nu(CO)$ and $E_{1/2}^{ox}$ in *cis*-$Mo(CO)_4L_2$).[16]

The consequence of electron withdrawal to the ligands in these formally ruthenium(II) complexes is sufficient to produce an electronic structure at the metal which at least superficially resembles that found for ruthenium(III). The complexes appear to represent a logical extension of earlier work showing the effects of metal to ligand electron withdrawal on the properties of Ru(II). The most profound effects occur in nitrosyl complexes where electron withdrawal leaves the

electron-deficient metal site in an electronic environment which resembles that of Ru(IV).[17]

The extent of intramolecular metal–ligand electron flow is expected to influence the reactivity of the complexes both at the metal and at the isocyanide ligand. The marked enhancement in Ru(III)/Ru(II) redox potentials relative to related couples has already been noted. Treatment of *cis*-[Ru(bpy)$_2$(CNCH$_2$Ph)$_2$](PF$_6$)$_2$ with PhCH$_2$NH$_2$ at room temperature or at reflux in acetonitrile solution failed to produce a carbene complex such as *cis*-[Ru(bpy)$_2$(C-(NHCH$_2$Ph)$_2$)$_2$](PF$_6$)$_2$. The isocyanide complexes do appear to react with stronger nucleophiles like sodium methoxide in methanol and these reactions are currently under investigation.

Reactions of *cis*-[Ru(bpy)$_2$(DME)](PF$_6$)$_2$ (1). The compound *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O is essentially insoluble in 1,2-dimethoxyethane (DME) although a very faint purple coloration of the solvent is apparent. Addition of silver(I) hexafluorophosphate to a stirred slurry of *cis*[Ru(bpy)$_2$Cl$_2$]·2H$_2$O in DME under nitrogen or argon results in a rapid reaction as indicated by the formation of a deep wine red color in solution. The reaction is complete within 5–10 min, but the subsequent filtration is facilitated if the mixture is stirred for 0.5–1.0 h in an inert atmosphere. The use of silver(I) perchlorate in place of AgPF$_6$ is not recommended since oxidation of the ruthenium occurs to some extent as indicated by the development of a dark green color in the solution. When stirring of the dark red solution is discontinued, the precipitated solid (AgCl) is removed by filtration in an inert atmosphere under gravity. The filtrate can be handled safely in an inert atmosphere. Addition of toluene or hexane precipitated dark red, tarry solids which did not redissolve easily in DME. The DME complex in DME solution appears to be quite stable in a clean, sealed system under argon (weeks) but otherwise decomposes more or less rapidly as indicated by a green deposit at the glass/solution interface.

Complex 1 is characterized by two bands in its electronic absorption spectrum at 491 and 342 nm. It has been possible to study reactions of 1 spectrophotometrically as described in the Experimental Section.

a. Reactions with Bidentate Ligands. Addition of 1 to a solution of bpy in DME results in an immediate color change to orange and formation of [Ru(bpy)$_3$]$^{2+}$ (λ_{max} 453 nm). In similar fashion, addition of 1 to 1,2-bis(diphenylphosphino)ethane (dppe) in THF gave [Ru(bpy)$_2$(dppe)]$^{2+}$ (λ_{max} 373 nm).[5c] The reaction is slow (hours) at room temperature and proceeds through an intermediate (λ_{max} 458 nm) which may perhaps be [Ru(bpy)$_2$(DME)(dppe)]$^{2+}$ in which both the DME and dppe ligands are monodentate.[18] At 60 °C, the production of [Ru(bpy)$_2$(dppe)]$^{2+}$ is much more rapid (minutes). When pure ethylenediamine (en) is added to 1, a rapid reaction occurs on mixing to produce [Ru(bpy)$_2$(en)]$^{2+}$ (λ_{max} 510, 358 nm).

b. Reactions with Monodentate Ligands. The reaction with PhCH$_2$NC has been described in detail. The addition of acetonitrile in excess to 1 at room temperature rapidly produces an intermediate (λ_{max} 469 nm) and then, more slowly, the complex *cis*-[Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ (λ_{max} 428) is formed. The formation of the bis(acetonitrile) complex is much more rapid at 60 °C or upon reversal of the order of addition. We believe that the absorption at 469 nm is produced by *cis*-[Ru(bpy)$_2$(DME)(MeCN)]$^{2+}$. Similar observations have been made for the reaction between 1 and pyridine (py). An intermediate is identified by an absorption at 480 nm and the final product of the reaction is *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (λ_{max} 456 nm). Further support for identification of the intermediate in this reaction as *cis*-[Ru(bpy)$_2$(DME)(py)]$^{2+}$ was obtained in the following manner. The stoichiometric 1:1 addition of pyridine to 1 was followed by the addition of Et$_4$NCl in

aqueous THF; on stirring of the mixture at room temperature, the formation of *cis*-[Ru(bpy)$_2$(py)Cl]$^+$ (λ_{max} 495 nm) was observed. Similarly when excess of an aqueous THF solution of NaNO$_2$ was added to the solution (λ_{max} 480 nm) of *cis*-[Ru(bpy)$_2$(DME)(py)]$^{2+}$ the final product was *cis*-[Ru(bpy)$_2$(py)(NO$_2$)]$^+$ (λ_{max} 458 nm, E_p^{ox} = 1.04 V). The reaction between 1 and an aqueous THF solution of NaNO$_2$ produces *cis*-[Ru(bpy)$_2$(NO$_2$)$_2$] (λ_{max} 464 nm, $E_{1/2}$ = 0.82 V).[3b]

Addition of a solution of NaOMe in MeOH to 1 gave *cis*-[Ru(bpy)$_2$(OMe)$_2$] (λ_{max} 570, 379 nm). In like manner, addition of LiPPh$_2$ in DME solution to 1 produces *cis*-[Ru(bpy)$_2$(PPh$_2$)$_2$] (λ_{max} 551, 377 nm, $E_{1/2}^{ox}$ = 0.32 V) which will be the subject of a detailed report. Finally, we note that 1 reacts rapidly at room temperature with tin(II) chloride in THF, with NaBH$_4$, with Na$_2$SO$_4$, and with *n*-butyllithium, but these reactions will be reported in greater detail later. Perhaps the most important point is that the DME complex, 1, has desirable versatility as a precursor in the synthesis of both charged and neutral ruthenium(II) complexes and may provide a route to compounds which have hitherto been inaccessible.

Registry No. 1, 69365-50-0; *cis*-[Ru(bpy)$_2$(CNCH$_2$Ph)$_2$](PF$_6$)$_2$, 69365-52-2; *cis*-[Ru(bpy)$_2$(CNC$_6$H$_4$OMe-4)$_2$](ClO$_4$)$_2$, 69365-54-4; *cis*-[Ru(bpy)$_2$(CNC$_6$H$_4$Cl-4)$_2$]$^{2+}$, 69365-55-5; *cis*-[Ru(bpy)$_2$Cl$_2$], 19542-80-4; *cis*-[Ru(bpy)$_2$(acetone)$_2$](ClO$_4$)$_2$, 69365-56-6; bpy, 366-18-7; dppe, 1663-45-2; en, 107-15-3; MeCN, 75-05-8; py, 110-86-1; NaNO$_2$, 7632-00-0; NaOMe, 124-41-4.

References and Notes

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(2) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978).
(3) See, for example: (a) W. L. Bowden, W. F. Little, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **97**, 6897 (1975); (b) D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1977.
(4) B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehman, and A. Ludi, *J. Am. Chem. Soc.*, **99**, 7368, (1977).
(5) (a) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, **16**, 42 (1963); (b) S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **11**, 994 (1972); (c) T. J. Meyer, D. J. Salmon, and B. P. Sullivan, *ibid.*, **17**, 3334 (1978).
(6) R. Appel, R. Kleinstuck, and K. D. Ziehn, *Angew. Chem., Int. Ed. Engl.*, **10**, 132 (1971).
(7) D. J. Doonan and A. L. Balch, *Inorg. Chem.*, **13**, 921 (1974).
(8) L. Malatesta, G. A. Padoa, and A. Sonz, *Gazz. Chim. Ital.*, **85**, 1111 (1955); L. Malatesta and G. A. Padoa, *Rend., R. Ist. Lomb. Sci. Lett.*, **91**, 227 (1957); W. Hieber and H. Heusinger, *J. Inorg. Nucl. Chem.*, **4**, 179 (1957); G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 256 (1977).
(9) J. Chatt, R. L. Richards, and G. H. D. Royston, *J. Chem. Soc., Dalton Trans.*, 1433 (1973); B. E. Prater, *J. Organomet. Chem.*, **34**, 379 (1972).
(10) D. F. Christian and W. R. Roper, *J. Organomet. Chem.*, **80**, C35 (1974).
(11) D. F. Christian and W. R. Roper, *Chem. Commun.*, 1251 (1971); J. A. McCleverty, D. Seddon, and R. N. Whitley, *J. Chem. Soc., Dalton Trans.*, 832 (1975).
(12) D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 458 (1972).
(13) T. J. Collins, K. R. Grundy, W. R. Roper, and S. F. Wong, *J. Organomet. Chem.*, **107**, C37 (1976).
(14) R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977).
(15) D. J. Salmon and B. P. Sullivan, unpublished results.

(16) J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972); M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, *ibid.*, 1743 (1973).
(17) R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **16**, 574 (1977).
(18) M. L. Brown, J. L. Cramer, J. A. Ferguson, T. J. Meyer, and N. Winterton, *J. Am. Chem. Soc.*, **94**, 8707 (1972); J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).

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Some Transition-Metal Chelates with 8-Amino-, 8-(Diphenylphosphino)-, and 8-(Diphenylarsino)quinoline Bidentate Ligands

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Bidentate ligands containing both nitrogen and either phosphorus or arsenic donor atoms are of special importance since they utilize both σ-donating and π-accepting atoms in the same ligand. These electronic effects make such ligands suitable for the stabilization of intermediate oxidation states of transition metals. We report here the synthesis and structure of some new coordination compounds of 8-(diphenylarsino)-, 8-(diphenylphosphino)-, and 8-aminoquinolines. These mixed-donor ligand systems have been particularly chosen for their stability and for the fact that their reactions with transition-metal ions have been little investigated. No complexes of 8-(diphenylarsino)quinoline (N-As) have been hitherto reported. The reactions of 8-(diphenylphosphino)-quinoline (N-P) with Ni(II) and Co(II) have been reported.[1] The reactions of 8-aminoquinoline (N-N) with several transition-metal ions have been investigated.[2] However, no complexes of (N-N) with ruthenium or rhodium have been reported. Moreover, attempts to isolate a complex of Pt(II) with (N-N) have failed.[2c] We investigated the reactions of (N-N) with Ru(II), Rh(III), Rh(I), and Pt(II) to fill this gap and to compare its behavior with that of the mixed-donor ligands.

Experimental Section

The ligands (N-As) and (N-P) were prepared by the reaction of 8-chloroquinoline with sodium metal and triphenylarsine and triphenylphosphine, respectively, in liquid ammonia.[3]

8-Aminoquinoline was prepared by the nitration of quinoline, separation of 8-nitroquinoline, and hydrogenation of this product.[4]

All complexes prepared by the procedures described below were dried under vacuum at 50 °C.

Complexes of (N-As)

(i) Dichlorobis(dimethyl sulfoxide)(8-(diphenylarsino)quino-line)ruthenium(II). To a suspension of 0.5 mmol of $Ru(Me_2SO)_4Cl_2$[5] in 10 mL of toluene was added a filtered solution of 0.5 mmol of (N-As) in 10 mL of toluene. The mixture was refluxed with continuous stirring for 2 h, during which the color changed to dark red and a light brown precipitate separated. The precipitate was filtered and washed with toluene and then with ether. The product decomposes at 265 °C. It is a nonelectrolyte in chloroform or nitrobenzene.

(ii) Trichloro(8-(diphenylarsino)quinoline)rhodium(III). To a filtered solution of $RhCl_3 \cdot 3H_2O$ (1.0 mmol) in 10 mL of H_2O was added a filtered solution of 1.0 mmol of (N-As) in 10 mL of acetone. The mixture was stirred at room temperature for 24 h. The orange-yellow precipitate that separated was filtered and washed with acetone and then with ether. It was recrystallized from chloroform as brown needles. It did not decompose or melt below 360 °C. The

product is a nonelectrolyte in chloroform or DMF. The product is diamagnetic; $\chi_M = -375 \times 10^{-6}$ at 25 °C.

(iii) Di-μ-chloro-bis{chlorocarbonyl(8-(diphenylarsino)quino-line)rhodium(II)}. To a filtered solution of $[Rh(CO)_2Cl_2]$ (0.5 mmol) in 10 mL of ethanol[6,7] was added a filtered solution of 0.5 mmol of (N-As) in 10 mL of 1:1 ethanol/acetone. The solution was refluxed with continuous stirring for 2 h. The orange-yellow precipitate which separated on cooling was filtered and washed with ethanol. The product melted at 250 °C. It is a nonelectrolyte in $CHCl_3$. Molecular weight by vaporimetry in $CHCl_3$: calculated for $[Rh(N-As)(CO)Cl_2]_2$, 1118; found, 999. μ eff = 2.17 μ_B at 25 °C.

(iv) Dichloro(8-(diphenylarsino)quinoline)palladium(II). To a filtered solution of $Pd(C_6H_5CN)_2Cl_2$ (0.5 mmol) in 10 mL of acetone was added a filtered solution of 0.1 mmol of (N-As) in 20 mL of acetone. Bright yellow crystals separated on standing. The product was filtered and washed with acetone; mp 330 °C with decomposition. The product is a nonelectrolyte in $CHCl_3$.

(v) Dichloro(8-(diphenylarsino)quinoline)platinum(II). To a filtered solution of 0.5 mmol of K_2PtCl_4 in 10 mL of H_2O was added a filtered solution of 0.5 mmol of (N-As) in 20 mL of acetone. An orange-yellow precipitate separated immediately. The mixture was stirred at room temperature for 1 h. The product was filtered and washed with acetone. The product decomposes at 315 °C. It is a nonelectrolyte in DMF.

Complexes of (N-P)

(i) Reaction of (N-P) with $Ru(Me_2SO)_4Cl_2$. The reaction of (N-P) with $Ru(Me_2SO)_4Cl_2$ was investigated under conditions similar to those described for the preparation of $Ru(Me_2SO)_2(N-As)Cl_2$. However, no Ru–(N-P) complex was obtained. Instead, the dimeric complex $Ru_2(Me_2SO)_5Cl_4$ was formed. The reaction was repeated without the addition of (N-P), and again $Ru_2(Me_2SO)_5Cl_4$ was obtained. The compound is orange-yellow; mp 250 °C with decomposition. It is a nonelectrolyte in $CHCl_3$ or nitrobenzene.

(ii) Dichloro(8-(diphenylphosphino)quinoline)rhodium(II). To a filtered solution of 1 mmol of $RhCl_3 \cdot 3H_2O$ in 10 mL of H_2O was added a solution of 1 mmol of (N-P) in 10 mL of acetone. A yellow precipitate separated immediately. It then dissolved on heating. The solution was refluxed for 24 h during which a pale yellow precipitate was obtained. The solvent was evaporated completely under reduced pressure. The yellow-orange residue was extracted with acetone from which it was then precipitated with ether. The product decomposes at 280 °C. It is a nonelectrolyte in $CHCl_3$ or nitrobenzene. μ_{eff} = 2.31 μ_B at 25 °C.

(iii) Di-μ-chloro-bis{chlorocarbonyl(8-(diphenylphosphino)quino-line)rhodium(II)}. To a filtered solution of 0.5 mmol of $[Rh(CO)_2Cl_2]^-$ in 10 mL of ethanol[6,7] was added a filtered solution of 0.5 mmol of (N-P) in 10 mL of ethanol. The solution was refluxed for 2 h. Half of the solvent was then evaporated under reduced pressure. Upon addition of diethyl ether, a pale yellow precipitate separated. It was filtered and washed with ethanol and then with ether; mp 150 °C with decomposition. The product is a nonelectrolyte in $CHCl_3$. μ_{eff} = 2.29 μ_B at 25 °C.

(iv) Dichloro(8-(diphenylphosphino)quinoline)palladium(II). To a filtered solution of 0.5 mmol of $Pd(C_6H_5CN)_2Cl_2$ in 10 mL acetone was added a filtered solution of 1 mmol of (N-P) in 10 mL of acetone. The mixture was stirred at 40–50 °C for 2 h, during which a yellow-orange precipitate separated. The product was filtered and washed with acetone; mp 230 °C with decomposition. The product is a nonelectrolyte in pyridine.

(v) Dichloro(8-(diphenylphosphino)quinoline)platinum(II). This compound was prepared by a method identical with that described above for the preparation of Pt(N-P)Cl₂. The product is yellow; mp 230 °C with decomposition. It is a nonelectrolyte in nitrobenzene.

Complexes of (N-N)

(i) Dichlorobis(dimethyl sulfoxide)(8-aminoquinoline)ruthenium(II). To a suspension of 1 mmol of $Ru(Me_2SO)_4Cl_2$ in 10 mL of toluene was added a filtered solution of 1 mmol of (N-N) in 10 mL of toluene. The mixture was refluxed for 2 h. The yellow-green product that separated was filtered and washed with toluene and then with ether; mp 200 °C with decomposition. The product is a nonelectrolyte in DMF.

(ii) Trichloro(8-aminoquinoline)rhodium(III). To a filtered solution of 2 mmol of (N-N) in 10 mL of acetone was added a filtered solution of 1 mmol of $RhCl_3 \cdot 3H_2O$ in 10 mL of H_2O. The mixture was refluxed