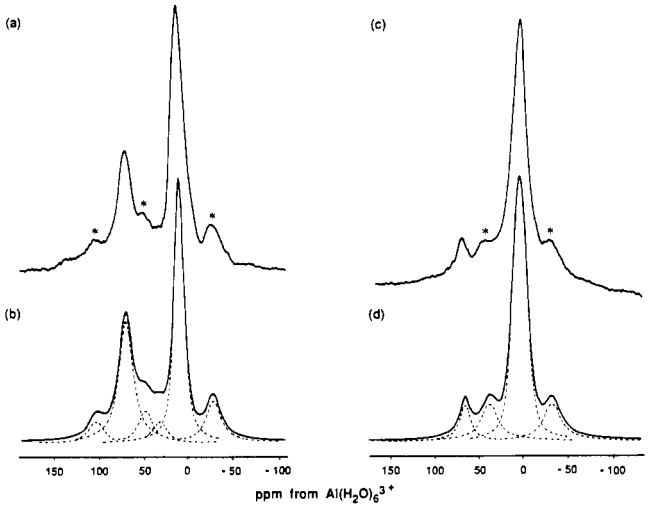

Figure 5. ^{27}Al MAS NMR spectra of pillared sodium trititanate: (a) As-prepared sample; (b) sample calcined at 500 °C. Asterisks denote spinning sidebands. The actual spectra are given above with their deconvolution given below.

has associated spinning sidebands, indicating the lowering of site symmetry. The spectrum is now identical with that of γ-alumina in every respect: chemical shift of the two species; octahedral-to-tetrahedral intensity ratio for aluminum; line-shape and sideband patterns.[17–19] We conclude that the Keggin ion pillars have become completely dehydrated to give alumina pillars according to the reaction[4]

$$n[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+} \rightarrow 6.5nAl_2O_3 + (7-x)H^+$$

Brønsted acidity is thus generated in the same way as is found in pillared smectite clays. The ^{27}Al MAS NMR spectra after calcination are very similar to those of pillared laponite.[20] The layered titanate structure expands to produce a microporous, thermally stable molecular sieve. The material offers potential as a shape-selective catalyst for selective NO_x processing and other important reactions. The structures of a number of layered oxides are similar to that of sodium tritanate, and they may therefore be amenable to permanent expansion.

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Registry No. $Na_2Ti_3O_7$, 12034-36-5; aluminum chlorohydrate, 1327-41-9; nitrogen, 7727-37-9.

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Chromatographic Separation and Characterization of Linkage Isomers of the 3-(Pyridin-2-yl)-1*H*-1,2,4-triazole Complex of Ruthenium(II) Bis(2,2′-bipyridyl)

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We are at present engaged in the investigation of the effect of the asymmetry of the ligands on the physical properties of ruthenium complexes containing ligands derived from 3-(pyridin-2-yl)-1*H*-1,2,4-triazole (HL1) (see Figure 1a).[2] Of particular interest are dinuclear compounds containing as the bridging ligand the anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (HL2) (Figure 1b) because, contrary to most of the previously used polypyridyl bridges, this ligand carries a negative charge and combines low π-acceptor ability with strong σ-donor properties.[3] In the dinuclear complexes the coordination of the $M(bpy)_2$ units is taking place at two different coordination sites. In addition to the pyridine ring the central triazole ring binds one metal center through N^2 and the other one through N^4. At present nothing is known about the coordinative differences between these two coordination sites. From Figure 1a it can be seen that two linkage isomers are possible for the compound $[Ru(bpy)_2(HL1)]^{2+}$, involving either coordination of the N^2 or the N^4 atom of the triazole ring. These isomers are, therefore, good model compounds for the investigation of the two coordination sites in HL2. In this contribution the separation of these isomers by semipreparative high-performance liquid chromatography (HPLC) is reported. They have been characterized by using NMR techniques, and their physical properties are reported. The relevance of the results obtained for the properties of the above-mentioned type of dinuclear compounds is discussed.

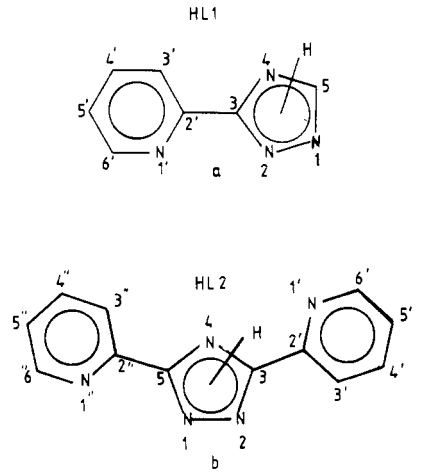

Figure 1. Structural formulas: (a) 3-(pyridin-2-yl)-1,2,4-triazole (HL1); (b) 3,5-bis(pyridin-2-yl)-1,2,4-triazole (HL2).

Experimental Section

An isomer mixture of $[Ru(bpy)_2(HL1)](PF_6)_2$ was prepared as reported in the literature.[2a] All solvents were of HPLC grade and used as received.

UV–visible spectra were recorded on a Shimadzu UV-240 spectrophotometer using matched 1-cm cells. Molar extinction coefficients are accurate up to 5%. Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer, equipped with a red-sensitive Hamamatsu R928 detector, using an emission slit width of 10 nm at room temperature and of 2.5 nm at 77 K and are not corrected for photomultiplier response. Electrochemical measurements were carried out by using an EG&G Par Model 174A polarographic analyzer with an EG&G Par 175 universal programmer. A saturated potassium calomel electrode (SCE) was used as a reference electrode. Cyclic voltammetry was carried out in Analar grade acetonitrile dried over molecular sieves, with 0.1 mol/L NEt_4ClO_4 as a supporting electrolyte, a glassy-carbon working electrode, and a scan rate of 100 mV/s. Preparative HPLC was carried out with a HPLC Technology RR 066 pump, adapted for semipreparative chromatography, together with an adapted ACS UV/VIS detector, a 1-cm^3 injector loop, and a Whatman Magnum 9 SCX 10-μm column. The mobile phase used was 80:20 acetonitrile/water containing 0.08 mol/L $LiClO_4$, with a flow rate of 5 mL/min and a detection

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Table I. Electronic and Electrochemical Data

compd	λ_{max} (log ϵ)	emission[b] λ_{max} (300 K)	emission[b] λ_{max} (77 K)	redox potentials (V vs SCE)[c] $Ru^{III/II}$	ligand based	
N^2 Isomer						
protonated	444 (4.11)	617	577	1.14	−1.49	−1.73
deprotonated	484 (4.04)	673	607	0.83	−1.49	−1.74
N^4 isomer						
protonated	452 (4.05)	616	580	1.20	−1.47	−1.72
deprotonated	488 (3.97)	665	607	0.90	−1.51	−1.78

[a] Measured in CH_3CN; λ_{max} in nm. [b] Spectra at room temperature measured in CH_3CN, and those at 77 K, in methanol; λ_{max} in nm. [c] Measured in 0.1 M TEAP/CH_3CN. For all measurements small amounts of HCl or NaOH were added to control the protonation process.

wavelength of 254 nm. The analytical HPLC system has been described in the literature.[4] Proton NMR spectra and nuclear Overhauser effect (NOE) spectra[5] were recorded on a Bruker 300-MHz spectrometer in $(CD_3)_2CO$; resonances were measured relative to $SiMe_4$. The spectra were recorded in $(CD_3)_2CO/D_2O$ (1:4), using DCl or NaOD to control the pH of the solution.

Results

With the use of preparative HPLC, amounts of up to 100 mg of the two deprotonated isomers were obtained. The purity of the isomers was checked on an analytical HPLC system. To the best of our knowledge this is the first time that coordination isomers of $Ru(bpy)_2$ compounds have been separated by using semipreparative HPLC techniques. The present work clearly shows the potential of the technique to obtain pure compounds that cannot be isolated by conventional column separation or by crystallization techniques.

To determine the coordination mode of the pyridyltriazole ligand in each of the isomers, ^1H NMR spectra were recorded. The spectra obtained for the protonated isomer 1 (retention time on the analytical column 9.1 min) and isomer 2 (retention time 12.1 min) are given in Figure 2. It can be seen that there are substantial differences in the spectra obtained for the two isomers. The electronic and electrochemical data of the isomers are listed in Table I. Table I shows the expected differences between the protonated and deprotonated compounds.[2]

Discussion

By the use of 2D COSY techniques and by comparison with assignments made for other similar compounds,[2,3,6] a complete assignment of the resonances was achieved.[7] However, for the present purpose an analysis of the triazole resonances is sufficient. For the compounds containing the protonated pyridyltriazole ligand, the triazole H^5 proton is found at 8.35 ppm in isomer 1 and at 8.68 ppm in isomer 2 (see Figure 2). In the deprotonated isomer 1 the triazole proton H^5 is found at 7.53 ppm, while for isomer 2 this resonance is found at 7.98 ppm. It is expected that H^5 is most strongly affected by the coordination mode of the ligand, as in the N^4 isomer this proton is directed to a neighboring bpy ring, while for the N^2 isomer this proton is not expected to interact with any other part of the molecule. As discussed before the $Ru(bpy)_2$-type compounds,[2,3,6] a large upfield shift of the H^6 protons of the bpy rings is observed. This has been explained by a diamagnetic anisotropic interaction of this proton with the ring currents of other bpy ligands. If we assume that a similar effect is found in the present species, which is expected on the basis of molecular models, then in isomer 1 the pyridyltriazole ligand is expected to be bound via the N^4 triazole nitrogen, while for isomer 2 the coordination mode is via N^2.

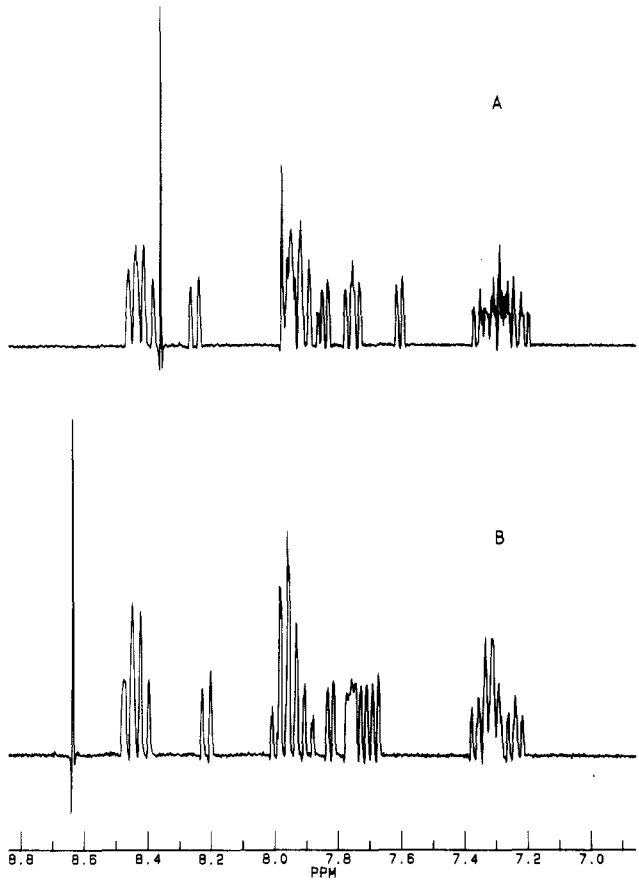

Figure 2. Proton NMR spectra of the protonated isomers: (A) isomer 1 (N^4), pH = 2.37; (B) isomer 2 (N^2), pH = 0.60.

To confirm this assignment nuclear Overhauser effect (NOE) experiments were carried out. It was found that upon irradiation of the H^5 triazole proton in the deprotonated isomer 1, an enhancement in bpy-based resonances at about 7.90 ppm was observed, while for isomer 2 upon radiation of the triazole proton no enhancement was observed in any part of the spectrum. NOE experiments carried out with the protonated compounds gave similar results. These results are in agreement with the assignment made above, as an NOE enhancement would only be expected for the N^4 isomer, where the triazole proton is close to a bpy ring.

For the protonated N^4 and N^2 isomers substantially different electrochemical and electronic data are observed. The higher Ru(II/III) redox potential observed for isomer 1, suggest that the N^4 coordination site is a weaker σ-donor than the N^2 position. This is further confirmed by the acidity of the two linkage isomers. Spectrophotometric titrations have shown that the triazole N–H proton in the N^2 isomer (in this species the proton will be on N^1 or N^4) is more acidic by 2 orders of magnitude (pK_a values of 4.07 and 5.95 for the N^2 and N^4 isomers, respectively).[8] This quite large difference in the pK_a values of the linkage isomers suggests that coordination of the triazole ring via the N^2 atom leads to a more substantial electron drain from the ligand to the metal center and again indicates that the N^2 atom is a stronger σ-donor than the N^4 atom. No substantial differences are observed between the emission energies of the two isomers.

As pointed out in the introduction, the N^4 and N^2 isomers are model compounds for the two coordination sites in the bridging ligand HL2. The absorption data in Table I suggest that, in the dinuclear compound, small but significant differences exist between the electronic properties of the two coordination sites. Also, since the difference between the Ru(II/III) redox potentials observed in the two isomers reported is only between 60 and 70 mV, it can

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be concluded that, in the dinuclear compound, either electrostatic effects or electron delocalization is responsible for the large, 300-mV separation of the ruthenium-based redox couples.

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Synthesis and Deprotonation Reactions of Neutral and Cationic Cyclic (Aminooxy)carbenes Derived from Platinum(II) Carbonyls

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Stable α-heteroatom-substituted (N, O, S) carbene complexes of platinum(II) have been prepared by either nucleophilic or electrophilic addition to a number of metal-coordinated ligands,[1] yet none have been reported from a carbon monoxide group. On the other hand, platinum group carbonyls are susceptible to nucleophilic attack, and their reactions with amines, alcohols, and water yield carbamoyl, alkoxy carbonyl, and hydroxy carbonyl complexes, respectively.[2]

Recent research work by Angelici and co-workers and some of us have been concerned with the reactions of 2-haloethanols, (2-haloethyl)amines, and the three-membered heterocycles $\overline{YCH_2CH_2}$ (Y = NH, O) with electrophilic carbonyl[3] and isocyanide[4] ligands to afford cyclic carbene complexes. In order to explore the generality of these reactions also with square-planar platinum(II) carbonyls, we report herein the synthesis and some deprotonation reactions of (aminooxy)carbene complexes derived from CO ligands.

Experimental Section

General Information. Experimental procedures and starting reagents were as previously reported.[4] IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer; ^{31}P NMR spectra were run on a Varian FT 80 A spectrometer. Melting points were determined on a hot-plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. The fast atom bombardment of **7** was obtained on a VG ZAB 2F instrument, operating with a Xe atom beam energy of 8 keV. The molecular weight measurements of **7** were taken on a Knauer osmometer at 36 °C with 1,2-dichloroethane as solvent. The complexes *cis*-$Cl_2(PPh_3)Pt(CO)$,[5] *cis*-$Cl_2(PMe_2Ph)Pt(CO)$,[5] *trans*-$[(PPh_3)_2ClPt(CO)]BF_4$,[2c] *trans*-$[(PPh_3)_2(CF_3)Pt(CO)]PF_6$,[6] and *trans*-$[(PPh_3)_2HPt(CO)]BF_4$,[6] were obtained as described in the literature.

Synthesis of *trans*-$[(PPh_3)_2Pt(\overline{COCH_2CH_2NH})X]BF_4$ [X = Cl (1a), Br (1b)]. These complexes were prepared by a procedure similar to that described herein for **1a**. To a stirring suspension of $Cl[NH_3CH_2CH_2Cl]$ (116 mg, 1.00 mmol) in THF (30 mL) at 0 °C was added aziridine (0.050 mL, 1.00 mmol) and then solid *trans*-$[(PPh_3)_2ClPt(CO)]BF_4$ (870 mg, 1.00 mmol). After 1 min, a solution IR spectrum revealed no ν(CO) absorption at 2121 cm^{-1} of the carbonyl complex. The reaction mixture was stirred at 0 °C for 30 min, and then stirring was continued for 3 h at room temperature to give a pale yellow suspension. The solution was taken to dryness under reduced pressure, and the residue was taken up with CH_2Cl_2 (20 mL). To the filtered solution was added dropwise *n*-hexane (80 mL) to give a white solid, which was filtered, washed with *n*-hexane (2 × 5 mL), and dried under vacuum: yield 685 mg, 75%; mp 242–244 °C dec. Anal. Calcd for $C_{39}H_{35}NClOP_2PtBF_4$: C, 51.68; H, 3.86; N, 1.53; Cl, 3.88. Found: C, 51.68; H, 3.80; N, 1.50; Cl, 3.92. Compound **1b** (45%) was obtained, together with **1a** (25%) and *cis*-$(PPh_3)_2PtCl(Br)$ (20%), by reaction of $Br[NH_3CH_2CH_2Br]$ (104 mg, 0.50 mmol), aziridine (0.024 mL, 0.48 mmol), and *trans*-$[(PPh_3)_2PtCl(CO)]BF_4$ (400 mg, 0.46 mmol) with the same experimental procedure reported for **1a**. The percentage yields were deduced by integration of the ^{31}P resonances of the product mixture. The complex *cis*-$(PPh_3)_2PtCl(Br)$ [dd, δ(P(trans to Cl)) 14.74 (d), $^1J_{PPt}$ = 3642 Hz; δ(P(trans to Br)) 12.30 (d), $^1J_{PPt}$ = 3660 Hz; $^2J_{PP}$ = 13.8 Hz] was identified by comparison with the ^{31}P NMR spectrum of a sample obtained on stirring *cis*-$(PPh_3)_2PtCl_2$ (269 mg, 0.34 mmol) and LiBr (15 mg, 0.17 mmol) in acetone (10 mL) at room temperature for 24 h.

***trans*-$[(PPh_3)_2Pt(\overline{COCH_2CH_2NH})Br]Br$ (1c).** A stirring suspension of $Br[NH_3CH_2CH_2Br]$ (100 mg, 0.49 mmol) in THF (20 mL) at 0 °C was treated with a 1.4 M *n*-hexane solution of *n*-BuLi (0.38 mL, 0.53 mmol). To the colorless solution was added solid *trans*-$[(PPh_3)_2PtCl(CO)]BF_4$ (200 mg, 0.23 mmol). A solution IR spectrum taken immediately revealed no ν(CO) absorption. The yellow reaction mixture was allowed to reach room temperature. Stirring was then continued for 2 days, during which time a pale yellow solid started to precipitate. Workup as for **1a** afforded 162 mg, 75%; mp 228–231 °C (dec). Anal. Calcd for $C_{39}H_{35}NBr_2OP_2Pt$: C, 49.28; H, 3.71; N, 1.47; Br, 16.81. Found: C, 48.93; H, 3.59; N, 1.43; Br, 16.40.

Similarly, compound **1a** was isolated by reaction of $Cl[NH_3CH_2CH_2Cl]$ (74 mg, 0.36 mmol) and *n*-BuLi (1.4 M in *n*-hexane, 0.26 mL, 0.36 mmol) with *trans*-$[(PPh_3)_2ClPt(CO)]BF_4$ (140 mg, 0.16 mmol) in THF (15 mL) after stirring for 1 day at room temperature: yield 130 mg, 92%.

***trans*-$[(PPh_3)_2Pt(\overline{COCH_2CH_2NH})(CF_3)]PF_6$ (2).** A stirring suspension of $Br[NH_3CH_2CH_2Br]$ (94 mg, 0.56 mmol) in THF (20 mL) at 0 °C was treated with aziridine (0.023 mL, 0.46 mmol), and then to the mixture was added solid *trans*-$[(PPh_3)_2Pt(CF_3)(CO)]PF_6$ (442 mg, 0.46 mmol). A solution IR spectrum revealed the immediate disappearance of the ν(CO) absorption at 2143 cm^{-1}. Stirring was continued for 24 h.

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