Mechanism I

$$\left.\begin{array}{l} (\eta^2\text{-}{}^{16}O_2)Fe + {}^{18}O_2 \xrightarrow{h\nu} Fe^{16}O^{18}O_2 + {}^{16}O \\ \underset{F}{(\eta^2\text{-}{}^{18}O_2)Fe} + {}^{16}O_2 \xrightarrow{h\nu} \underset{G}{Fe^{16}O_2{}^{18}O} + {}^{18}O \end{array}\right\} \quad (8)$$

Mechanism II

$$\left.\begin{array}{l} (\eta^2\text{-}{}^{16}O_2){}^{18}O_2FeCO \xrightarrow{h\nu} Fe^{16}O_2{}^{18}O + {}^{18}OC^{16}O \\ \underset{E}{(\eta^2\text{-}{}^{18}O_2){}^{16}O_2FeCO} \xrightarrow{h\nu} \underset{G}{Fe^{16}O^{18}O_2} + {}^{16}OC^{18}O \end{array}\right\} \quad (9)$$

4. Conclusions

Our experiments provide persuasive spectroscopic evidence that two binary iron oxides are generated by prolonged UV photolysis of iron pentacarbonyl trapped in an O_2-doped argon matrix. The products in question are $(\eta^2\text{-}O_2)Fe$ and FeO_3 with the structures II and XXVIII, respectively. Hence we have been able to complete our analysis of the steps which take place as photooxidation proceeds, via a variety of oxoiron carbonyl intermediates (A–E), first to $(\eta^2\text{-}O_2)Fe$ and ultimately to FeO_3, while all the CO originally coordinated to the metal center is converted in the end to CO_2. Scheme I presents a mechanism which takes account of all the photoproducts reported in parts 1[2] and 2 of this investigation.

The results reported here, relating to the final stages of the photooxidation of iron pentacarbonyl, invite obvious comparisons with earlier experiments in which iron atoms were cocondensed with oxygen or oxygen/argon mixtures.[21–23] The earlier studies brought to light IR absorptions with wavenumbers virtually identical to those we assign to the absorbers $(\eta^2\text{-}O_2)Fe$ and FeO_3, but the spectra were interpreted rather differently. Certainly our results are consistent with, and lend support to, the earlier characterization of the peroxide $(\eta^2\text{-}O_2)Fe$.[21] On the other hand, our analysis must cast some doubt on the identification of FeO_2[21–23] as the source of the absorption near 945 cm^{-1}.

It is of interest to compare the binary metal oxides produced by the matrix photooxidation of different metal carbonyls, viz. $Fe(CO)_5$, $Cr(CO)_6$,[6] $Mo(CO)_6$,[5] $W(CO)_6$,[5] and $Mn_2(CO)_{10}$.[38] The group 6 carbonyls show a progressive trend in which the +6 oxidation state seems to be more readily attained in the sequence Cr < Mo < W. Thus, $Cr(CO)_6$ yields CrO_2 as the ultimate oxidation product,[6] whereas $Mo(CO)_6$ gives a mixture of MoO_2 and MoO_3, with MoO_2 being converted gradually to MoO_3 on prolonged broad-band irradiation.[5] By contrast, the photooxidation of $W(CO)_6$ gives no vestige of WO_2, except in the coordinated form of derivatives like $O_2W(CO)_n$ (n = 2 or 4);[3–5] instead WO_3 is the final product, and this in turn evolves from another tungsten(VI) derivative $(\eta^2\text{-}O_2)WO_2$. In view of the behavior of $Cr(CO)_6$, it may come as a surprise that $Mn_2(CO)_{10}$ is oxidized ultimately to Mn_2O_7.[38] However, thermodynamic considerations are by no means the only factor determining the nature of the ultimate products in these reactions. Because the experiments entail long periods of broad-band photolysis, the outcome is likely to hinge on the photolability of the different products, notably in relation to the characteristics of the photolyzing radiation. Thus, the apparent stability of FeO_3, under conditions which will not support CrO_3,[6] may well reflect a fortuitous lack of coincidence between its optical absorption properties and the principal regions of emission of the photolysis sources used in our experiments.

The detection of FeO_3 raises also the teasing question of whether the iron analog of the tetraoxides RuO_4 and OsO_4 might also be amenable to matrix synthesis. Recent reports claim that this compound can in fact be generated either by disproportionation of ferrate(VI) or by electrochemical means.[39] With the incorporation into a solid cryogenic matrix of an oxidant more powerful and photolabile than dioxygen, e.g. O_3, and the adoption of more selective conditions of photolysis, it may be feasible to devise alternative access to FeO_4.

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Notes

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Irreversible Addition of Arenediazonium Ligands to a Pt–Pt Bond. Solid-State Structure of $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$

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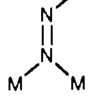
Introduction

The chemistry of arenediazonium complexes has attracted a great deal of attention,[1] but only a small fraction of studies involves coordination of the arenediazenido (ArN_2) ligand to dinuclear complexes in a bridging position. Four different structural types (I–IV) have been characterized.[2]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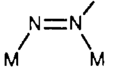
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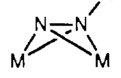
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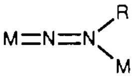
IV

Although the reactivity of diazonium salts with several metal derivatives containing dppm (dppm = $Ph_2PCH_2PPh_2$) as a bridging ligand has been previously reported,[3–6] the only structural

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Table I. NMR Data[a] for **1** and **2a–c**

complex	^{1}H NMR[b,c]	^{31}P{^{1}H} NMR[d]
1	4.41 (br m)[e]	5.9, $^1J(\mathrm{PtP}) = 2950$
2a	3.14 (m, H_A), 2.79 (d "qn", H_B), $J(H_AH_B) = 14.0$, $J(PH_A) = 3.6$, $J(PH_B) = 4.8$	5.2 (m, P_A), 0.2 (m, P_B), $^1J(\mathrm{PtP_A}) = 2902$, $^1J(\mathrm{PtP_B}) = 2880$
2b	2.97 (m, H_A), 2.66 (d, "qn", H_B), $J(H_AH_B) = 14.0$, $J(PH_A) = 3.5$, $J(PH_B) = 5.0$, $^3J(\mathrm{PtH_A}) \approx 50$	5.7 (m, P_A), 0.5 (m, P_B), $^1J(\mathrm{PtP_A}) = 2960$, $^1J(\mathrm{PtP_B}) = 2910$
2c	3.72 (s, OCH_3), 2.85 (m, H_A), 2.66 (d "qn", H_B), $J(H_AH_B) = 13.8$, $J(PH_A) = 3.6$, $J(PH_B) = 5.0$	6.1 (m, P_A), 1.0 (m, P_B), $^1J(\mathrm{PtP_A}) = 2992$, $^1J(\mathrm{PtP_B}) = 2948$

[a] δ in ppm, J in hertz. Abbreviations: d, doublet; m, multiplet; qn, quintet; s, singlet. [b] In CD_2Cl_2 at 300.13 MHz. $J(PH) = |^2J(PH) + {}^4J(PH)|$. [c] Phenyl resonances not reported. [d] In CH_2Cl_2/acetone-d_6 (20%) at 121.5 MHz. [e] From ref 7a.

study deals with a rather unusual diazadicobaltatetrahedrane unit.[6]

Here we report the syntheses and characterizations of the new series of cations $[Pt_2Cl_2(dppm)_2(N_2C_6H_4X)]^+$ (where X = OCH_3, F, NO_2). The X-ray crystal structure of $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$ shows the presence of a μ-η^1-N=NAr bridge.

Results and Discussion

Arenediazonium salts $[p\text{-}XC_6H_4N_2][BF_4]$ (X = NO_2, F, OCH_3) irreversibly react with $[Pt_2Cl_2(\mu\text{-dppm})_2]$[7] (**1**) in acetone at 20 °C, yielding air-stable solutions of compounds **2** (eq 1).

$$\underset{\mathbf{1}}{Pt_2Cl_2(\mu\text{-dppm})_2} \xrightarrow{p\text{-}XC_6H_4N_2^+BF_4^-} [Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4X)]BF_4 \quad (1)$$

$$\begin{array}{l} \mathbf{2a},\ X = NO_2 \\ \mathbf{b},\ X = F \\ \mathbf{c},\ X = OCH_3 \end{array}$$

All complexes are air-stable solids that completely dissolve in dichloromethane and are moderately soluble in acetone and chloroform. Conductivity values of **2a–c** account for 1:1 electrolytes (see Experimental Section).

Although the IR spectra of **2a–c** do not exhibit any bands that can be unambigously assigned to ν(NN), the presence of the inserted ligand is shown by NMR spectroscopy. Spectral parameters are given in Table I.

In addition to the expected resonances due to the phenyl protons (P–Ph and N–Ar), the ^{1}H NMR spectra of **2a–c** show two resonances in the PCH_2P region with the characteristic AB pattern. Each resonance appears as a doublet of pseudoquintets (due to virtual coupling to four P nuclei), the high-field signal always being more resolved than the other one. The inequivalence of the two protons in each dppm methylene group is typical of the ^{1}H NMR spectra of several "A-frame" complexes.[8] Each methylene proton signal should show further splitting due to isotopomers containing ^{195}Pt. However, only for the low-field signal is there some evidence of platinum satellites. At 300 MHz these take the form of broad humps, and a ^3J(PtH) value at 50 Hz was roughly estimated for **2b** alone (Table I). Whereas chemical shift anisotropy relaxation is the most reasonable cause of broadening in ^{195}Pt satellites,[9] methylene resonances with absent or reduced PtH coupling are not unusual for dppm–platinum A-frames.[5,8a–c,10] The *p*-OCH_3 resonance in **2c** occurs at 3.72 ppm.

Table II. Crystallographic Data for $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$

formula	$C_{57}H_{51}BCl_2F_4N_2OP_4Pt_2$
fw	1451.8
space group	*Pbcm*
a, Å	11.828 (3)
b, Å	17.926 (4)
c, Å	28.025 (6)
V, Å^3	5492 (2)
Z	4
ρ_{calc}, g cm^{-3}	1.623
T, K	295
λ, Å	0.710 73
μ(Mo Kα), cm^{-1}	50.00
range of transm factors	1.016–0.972
$R(F_o)$[a]	0.063
$R_w(F_o)$[b]	0.065
GOF[c]	1.31

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w^{-1} = \sigma(F_o)^2 + 0.002(F_o)^2$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

Table III. Selected Positional Parameters for $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$

atom	*x*	*y*	*z*	10^3U(eq),[a] Å^2
Pt(1)	0.1931 (1)	0.2148 (1)	0.2500	32 (1)
Pt(2)	−0.0565 (1)	0.1418 (1)	0.2500	29 (1)
Cl(1)	0.3872 (7)	0.2061 (5)	0.2500	57 (3)
Cl(2)	−0.1437 (7)	0.0265 (4)	0.2500	45 (3)
P(1)	0.1866 (5)	0.2139 (5)	0.1673 (2)	36 (2)
P(2)	−0.0609 (5)	0.1509 (3)	0.1670 (2)	38 (2)
N(1)	0.0258 (22)	0.2331 (13)	0.2500	40 (9)
N(2)	0.0057 (20)	0.3004 (12)	0.2500	36 (8)
O	−0.4160 (18)	0.4427 (11)	0.2500	64 (9)
C(31)	0.0439 (17)	0.2220 (10)	0.1462 (7)	37 (7)
C(32)	−0.5190 (35)	0.4041 (30)	0.2500	123 (26)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Parameters for $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)]BF_4$

Bond Distances (Å)			
Pt(1)–Pt(2)	3.229 (2)	Pt(1)–N(1)	2.006 (26)
Pt(1)–P(1)	2.320 (5)	Pt(2)–N(1)	1.904 (24)
Pt(2)–P(2)	2.331 (5)	N(1)–N(2)	1.230 (32)
Pt(1)–Cl(1)	2.308 (8)	P(1)–C(31)	1.794 (20)
Pt(2)–Cl(2)	2.310 (8)	P(2)–C(31)	1.873 (19)
O–C(4)	1.39 (4)	O–C(32)	1.40 (5)
Bond Angles (deg)			
P(1)–Pt(1)–P(1′)	176.1 (3)	P(2)–Pt(2)–P(2′)	171.6 (3)
Cl(1)–Pt(1)–N(1)	174.5 (7)	Cl(2)–Pt(2)–N(1)	175.8 (8)
P(1)–Pt(1)–N(1)	88.2 (1)	P(2)–Pt(2)–N(1)	87.2 (1)
P(1)–Pt(1)–Cl(1)	91.9 (1)	P(2)–Pt(2)–Cl(2)	93.0 (1)
N(2)–N(1)–Pt(1)	110.5 (19)	N(2)–N(1)–Pt(2)	138.1 (22)
Pt(1)–N(1)–Pt(2)	111.4 (12)	N(1)–N(2)–C(1)	120.6 (23)
Pt(1)–P(1)–C(31)	111.1 (6)	Pt(2)–P(2)–C(31)	110.1 (6)
P(1)–C(31)–P(2)	117.7 (10)	C(4)–O–C(32)	118.4 (28)

The ^{31}P{^{1}H} NMR spectra of **2a–c** show the expected pattern for the AA′BB′ spin system (with superimposed AA′BB′X and AA′BB′XX′ components), which accounts for two inequivalent pairs of P nuclei.

Conclusive evidence of the unsymmetrical nature of the species and the presence of a coordinated ArN_2 ligand in **2a–c** was

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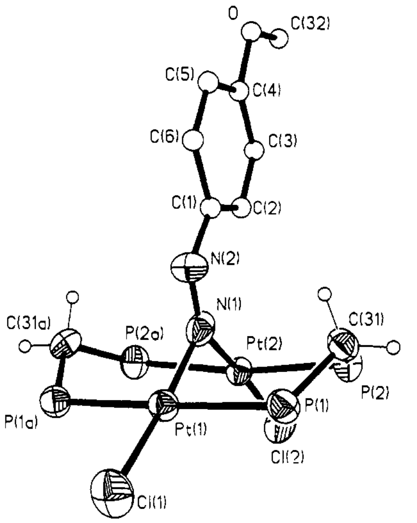

Figure 1. Perspective view of the cation of **2c** with the numbering scheme. Thermal ellipsoids are shown at the 30% level. Phenyl rings have been omitted for clarity.

achieved by a crystal structure determination of **2c**. X-ray-quality crystals of **2c** were obtained from a CH_2Cl_2 solution. Crystallographic parameters are summarized in Table II. Selected positional parameters are reported in Table III. An abbreviated list of bond lengths and angles is given in Table IV.

No significant interionic contacts were observed. The cation (Figure 1), with C_s site symmetry, reveals an almost regular A-frame structure with terminal chloride and bridging dppm ligands. The two Pt centers have nearly square-planar geometries, the most noticeable deviation being the P–Pt–P angle of 171.6 (3)° at Pt(2). The pseudo-six-membered $Pt_2P_4C_2$ ring has the "boat" conformation, and no significant twist of the P–Pt–P vectors is present, as is evidenced by the small value of the P(1)–Pt(1)–Pt(2)–P(2) torsion angle (3.78 (20)°). The metal–metal separation of 3.229 (2) Å is clearly nonbonding and comparable to that found in the isoelectronic nitrosyl analogues $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-NO})]BF_4$ (Pt–Pt = 3.186 (2) Å)[10a] and $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-NO})]BPh_4$ (Pt–Pt = 3.246 (3) Å).[10b]

The arenediazenido ligand occupies the bridging apical site of the A-frame arrangement, with nearly similar Pt–N distances (Pt(1)–N(1) = 2.006 (26) Å, Pt(2)–N(1) = 1.904 (24) Å). The Pt–N–N angles exhibit a more pronounced asymmetry (Pt(1)–N(1)–N(2) = 110.5 (19)°, Pt(2)–N(1)–N(2) = 138.1 (22)°). Although to a lower extent, a similar degree of asymmetry of the arenediazonium bridge has been observed in $Mn_2(CO)_8(\mu\text{-}\eta^1\text{-}N_2Ph)$, wherein Mn–N(1)–N(2) = 134.5 (1)° as opposed to Mn′–N(1)–N(2) = 119.5 (1)°.[11] The N═NAr group is bent at the β-nitrogen (N(1)–N(2)–C(1) = 120.6 (23)°), and the N(1)–N(2) distance of 1.230 (32) Å is consistent with an N═N double-bond character. Similar values have been reported for the N–N bond distance in $Mn_2(CO)_8(\mu\text{-}N_2Ph)$ (1.233 (2) Å),[11] $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)$ (1.238 (18) Å),[2f] and $Ru_3(CO)_9(\mu\text{-dppm})(\mu\text{-}N_2C_6H_3Cl_2\text{-}2,4)$ (1.230 (5) Å).[2b] The latter complexes are all examples of $\mu\text{-}\eta^1$ ArN_2 coordination.

Compounds **2** are stable toward substitution of the bridging arenediazenide. Thus, dichloromethane solutions of **2** are unreactive toward CO under mild conditions. In contrast, carbon monoxide can be easily replaced in $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CO})]$[12] by $ArN_2^+X^-$ to give complexes **2** in high yield (see Experimental Section). Attempts to protonate **2** were unsuccessful. Their orange dichloromethane solutions turned dark orange to red upon treatment with $HBF_4{\cdot}Et_2O$ either at room temperature or at −20 °C. The color change, however, is not permanent (even with a large excess of $HBF_4{\cdot}Et_2O$), and solutions turn orange on standing. Starting materials were always recovered upon precipitation. This behavior is not uncommon, since protonation on N_β in complexes of type I has been seldom reported.[2c,13]

Experimental Section

General Data. All experiments were performed under a dry nitrogen atmosphere. Bis(diphenylphosphino)methane (Aldrich), tetrafluoroboric acid–diethyl ether complex (Fluka AG), *p*-nitrobenzenediazonium tetrafluoroborate (Aldrich), *p*-methoxybenzenediazonium tetrafluoroborate (Aldrich), and CO gas (J. T. Baker) were used as received. *p*-Fluorobenzenediazonium tetrafluoroborate,[14] $[Pt_2Cl_2(\mu\text{-dppm})_2]$,[7] and $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CO})]$[12] were prepared according to the literature. NMR chemical shifts (in ppm) are referenced to internal TMS (^1H) and to external 85% H_3PO_4 (^{31}P). Analyses were performed by the Microanalysis Laboratory of our department.

Preparation of $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)]BF_4$ (2b). A solution of a 5-fold molar excess of $[p\text{-}FC_6H_4N_2][BF_4]$ in acetone (4 mL) was added to a suspension of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (100 mg, 0.0813 mmol) in acetone (6 mL). Immediately, an orange solution was obtained, which was stirred for 30 min. The solvent was then removed under reduced pressure, and the solid residue was partially redissolved in CH_2Cl_2. The unreacted benzenediazonium salt was recovered as an insoluble material and filtered off. Addition of diethyl ether to the filtrate gave an orange precipitate, which was filtered, washed with ether, and dried in vacuo; yield 83 mg (72%). Mp: 290–292 °C. Anal. Calcd for $C_{56}H_{48}BCl_2F_5N_2P_4Pt_2$: C, 47.17; H, 3.39; N, 1.96. Found: C, 46.20; H, 3.41; N, 1.87. Equivalent conductance (CH_2Cl_2, 20 °C, 7×10^{-4} M): 46.4 Ω^{-1} mol^{-1} cm^2.

The complexes **2a,c** were synthesized in a similar way, and their preparation is not reported in full detail. The color, isolated yield, melting point, equivalent conductance, and analytical data are summarized as follows.

2a: Orange solid, 86%, 243–245 °C, 36.7 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{56}H_{48}BCl_2F_4N_3O_2P_4Pt_2$: C, 45.85; H, 3.29; N, 2.86. Found: C, 44.87; H, 3.23; N, 2.25.

2c: Yellow orange solid, 82%, 280–283 °C, 45.6 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{57}H_{51}BCl_2F_4N_2OP_4Pt_2$: C, 47.16; H, 3.54; N, 1.93. Found: C, 46.28; H, 3.52; N, 1.91.

Reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CO})]$ with $[p\text{-}NO_2C_6H_4N_2][BF_4]$. The complex $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CO})]$ (75 mg, 0.06 mmol) was suspended in acetone (8 mL), and a solution of the diazonium salt (71 mg, 0.3 mmol) in acetone (5 mL) was added by cannula. The suspension immediately cleared, and the resulting deep orange solution was stirred for 30 min. An orange solid was isolated as above reported for **2b**. The infrared spectrum of the product does not show any band assignable to a carbonyl stretching, whereas stretches at 1518 and 1340 cm^{-1} can be attributed to the nitro group. The $\nu(BF_4)$ band occurs as a broad band at 1050 cm^{-1}. NMR characterization helped to identify the reaction product as complex **2a**. Yield: 78%.

Complexes **2b,c** may be prepared in the same way, starting with the appropriate diazonium salt.

Structure Analysis. X-ray measurements were made at room temperature (22 °C) with molybdenum radiation (λ = 0.71073 Å), on a Siemens R3m/V four-circle diffractometer. Intensity data were collected with the ω-scan method from an orange crystal of dimensions 0.21 × 0.90 × 0.12 mm. The unit cell dimensions were determined by refinement of the setting angles of 40 accurately centered reflections in the $14° < 2\theta < 30°$ range. Systematic absences are consistent with *Pbcm* and *Pca*2$_1$ space groups. The intensities of 4625 unique reflections were measured; 2695 of these were used in subsequent calculations ($I > 3\sigma(I)$). The positions of the Pt and P atoms were determined from a Patterson map; the structure was completed by difference Fourier syntheses. The successful solution of the structure confirmed the choice of *Pbcm* for space group to be correct. An absorption correction was applied (DIFABS).[15] The Pt, Cl, P, N, O, methylic-C, and methylenic-C atoms and those ring carbon atoms with high thermal parameters were anisotropically refined. The hydrogen atoms were included in their idealized position (d(C–H) = 0.96 Å) with their isotropic thermal parameters set at 0.08 Å^2. The fluorine atoms of the BF_4^- anion are disordered, and a satisfactory geometry for the anion could not be obtained. Additionally, the site-occupation factors of the fluorine atoms were fixed at 0.5, and the whole anion was refined isotropically. The ranges of B–F bond lengths and F–B–F angles are 1.27–1.73 Å and 62–123°, respectively. The final full-matrix least-squares refinement converged at R = 0.063 and R_w =

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0.065 for 238 parameters. The highest peak in the final difference Fourier map had a value of 1.55 e Å^{-3}, 1.58 Å from Pt(2). All calculations were performed with the Siemens SHELXTL PLUS (MicroVAX II) and PARST[16] programs. Atomic scattering factors and anomalous dispersion terms used were those supplied in the Siemens structure determination package.

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Supplementary Material Available: Figures showing an ORTEP diagram of **2c** and selected NMR spectra (Figures S1-S3) and full tables listing crystallographic and data collection parameters (Table SI), atomic coordinates (Table SII), bond lengths and angles (Tables SIII and SIV), anisotropic thermal parameters (Table SV), and hydrogen atom coordinates (Table SVI) (12 pages); a listing of calculated and observed structure factors (Table SVII) (17 pages). Ordering information is given on any current masthead page.

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A Tridecanuclear Ruthenium(II)-Polypyridine Supramolecular Species: Synthesis, Absorption and Luminescence Properties, and Electrochemical Oxidation

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Continuing our studies on the synthesis and characterization of metal complexes of high nuclearity,[2] we have prepared the luminescent and redox-active tridecanuclear Ru(II)-polypyridine supramolecular species $\mathrm{Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3^{26+}}$ (**1**) schematically represented in Figure 1 (2,3-dpp = 2,3-bis(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine).[3]

The novel tridecanuclear species **1** has been obtained by using the "complexes as ligand and complexes as metals" synthetic strategy illustrated in Figure 2, i.e., by reacting a $\mathrm{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)(2,3\text{-dpp})]_3^{8+}}$ core (**2**),[2d] which contains three free chelating sites that can play the role of ligands, with three $\mathrm{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2^{4+}}$ units (**3**),[2f] which contain easily replaceable $\mathrm{Cl^-}$ ligands and can thus play the role of metals. The building blocks **2** and **3** are both well-characterized species that can be obtained as $\mathrm{PF_6^-}$ salts.[2d,f,g,i,j]

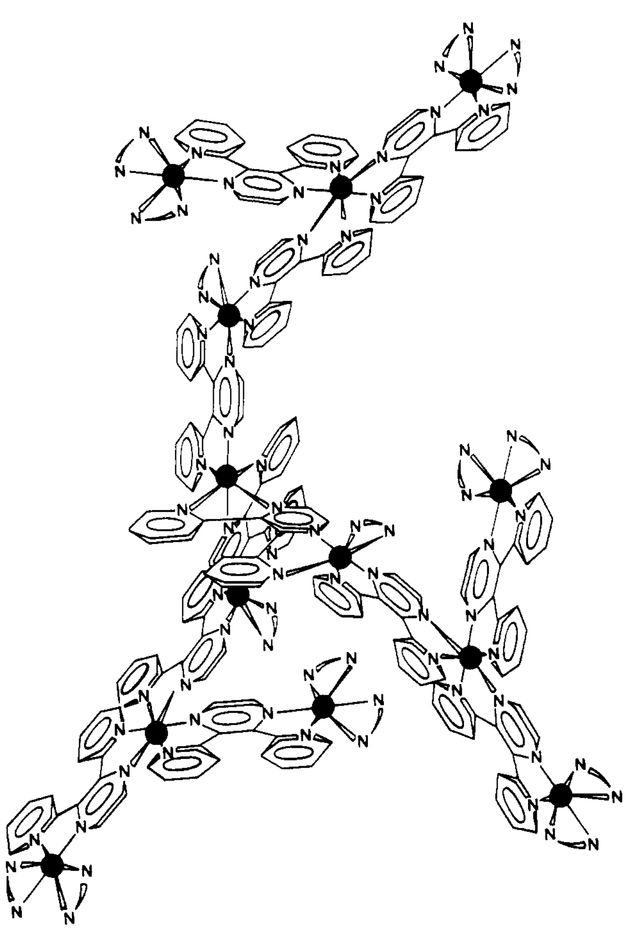

Figure 1. Schematic representation of the tridecanuclear complex **1**. N-N stands for bpy.

Experimental Section

The reaction illustrated in Figure 2 has been carried out as follows. To a solution of $\mathrm{\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2\}(PF_6)_4}$ (0.036 g, 0.018 mmol) in 2:1 (v/v) methanol-water (3 mL) was added solid $\mathrm{AgNO_3}$ (0.006 g, 0.004 mmol). After 3 h of stirring at room temperature, $\mathrm{\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)(2,3\text{-dpp})]_3\}(PF_6)_8}$ (0.020 g, 0.006 mmol) and ethylene glycol (3 mL) were added and the mixture was refluxed for 7 days. After removal of AgCl by repeated centrifugation, an excess of solid $\mathrm{NH_4PF_6}$ was added to the mother liquor, and the violet solid thus obtained was filtered out. The product was purified by size-exclusion chromatography on Sephadex G-50 (acetonitrile eluant). From the eluant, the product was recovered as a violet powder by addition of ethanol and partial evaporation in vacuo. Yield after purification: 0.043 g (70%). Anal. Calcd. for $\mathrm{C_{318}H_{240}F_{156}N_{78}P_{26}Ru_{13}\cdot 10H_2O}$: C, 36.06; H, 2.51; N, 10.48. Found: C, 36.01; H, 2.48; N, 10.03. The infrared spectrum shows the characteristic bands of bridged 2,3-dpp,[2e] whereas the bands of unbridged 2,3-dpp[2e] are not present, indicating that only a 1:3 combination of **2** and **3** (Figure 2) has occurred. It should also be noted that the building blocks **2** and **3** display absorption, luminescence, and electrochemical properties clearly distinct from those of **1**, and this would also be the case for hypothetical side products containing $\mathrm{Cl^-}$ ligands as **3** and/or unsaturated chelating sites as **2**.[2e,j]

The equipment used for spectroscopic, photophysical, and electrochemical measurements has been previously described.[2]

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