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Synthesis, Stability, and Crystal Structure of an Azulenium Cation Containing an Adamantyl Group

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Starting from the trimethylsilyl enol ether of 1-acetyl-1,3,5cycloheptatriene, the title 1*H*-azulenium cation was synthesized by a five-step sequence that involved a Noyori–Mukaiyama aldol reaction, a Nazarov cyclization, a Shapiro reaction, and a hydride abstraction. The Nazarov reaction of the aldol-type adduct resulted in the formation of an unusual double-bond position isomer, which has never been obtained in similar reactions forming tetrahydroazulenones. The pK_R^+ value of the title cation was found to be 9.8, which is less than that expected by inductive stabilization from the number of carbons at the 1-position. The X-ray crystal structure of the title cation (ClO_4^- salt) reveals CH–O interactions and deformation of the azulenyl ion part.

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Introduction

The tropylium cation (1) has played an important role in the historical development of positively charged Huckeloid aromatic systems.^[1,2] The stability of cyclic π -conjugated carbocations, particularly as expressed in pK_{R}^{+} values, aids in understanding the capability of π -conjugation and the outcome of various structural effects on delocalized carbocations. We previously reported the syntheses of various 1,1-spiro-alkylated 1*H*-azulenium cations $2-6^{[3,4]}$ and 1,1dialkylated 1*H*-azulenium cations $7-9^{[5]}$ (Figure 1). Their pK_{R}^{+} values were in the range of 8.6–13.2, which are far greater than that $(3.9)^{[6]}$ of 1. The enhanced thermodynamic stability is attributable to the stabilization of both the inductive and σ - π conjugation effects of the exocyclic ring at the 1-position and the π - π conjugation of the double bond at the 2,3-positions. The order of stability of the mono-spiroalkylated cations increases with the number of carbons of the exocyclic ring, as 2 < 3 < 4.^[3] On the other hand, the order of stability of the dialkylated cations does not correspond with the number of carbons of the alkyl groups at the 1-position, as 7 < 9 < 8.^[5] Since the degree of π - π conjugation is the same in a series of the cations, the order of stability of these cations should also correspond to the degree of substitution at the 1-position. In other words, the cations having more carbons in the substituent at the 1-

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position should be more stable, although the effects may saturate at some large number of carbons. The reason for the stability of 7-9, which is not compatible with the number of carbons in the alkyl groups, may be ascribed to the relative difficulty of solvation of 9 due to congestion around the 1-position by two slightly bulkier propyl groups. Therefore, in order to increase the stability of 1,1-substituted azulenium cations by an inductive effect, the introduction of a compact substituent with a larger number of carbons is required. Considering this, we designed the



Figure 1. Tropylium and azulenium ions with various spiro-carbocycles.



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azulenium cation **10**, containing an adamantyl group constructed with ten carbons. In this paper, we describe its synthesis, stability, and X-ray structural analysis.

Results and Discussion

The title cation was synthesized by the method that we had developed for synthesizing spiroalkylated cation 3 and 4 (Scheme 1).^[3b,5,7] The Noyori–Mukaiyama aldol reaction^[8] of trimethylsilyl enol ether 11 with 2,2-dimethoxyadamantane in the presence of trimethylsilyl triflate gave 12 in 44% yield. The subsequent Nazarov cyclization^[9,10] provided azulenone 13 in 50% yield. The azulenone 13 was transformed into the 1,4-dihydroazulene 14 via the tosylhydrazone of 13 by the Shapiro reaction.^[11] A final hydride abstraction from 14 with trityl perchlorate resulted in the desired cation 10 as yellowish brown crystals. The structure of 10 was characterized by spectroscopic and combustion analyses. All signals except unresolved peaks for hydrogens in the ¹H NMR spectrum of **10** were assigned by analysis of H-H COSY and NOE experiments (Figure 2). The chemical shifts of the olefinic protons of 10 along with those of 2, 3, and 4 are listed in Table 1. The protons at the 2- and 8-positions of 10 resonate at a lower magnetic field than that those of 2, 3, and 4. In addition, the axial H_a and H_b of the adamantyl group show similar NOEs with H-2 and H-8, respectively, as was observed in 12, 13, and 14, suggesting a steric compression effect^[12] between H_a and H-2 and between H_b and H-8. The UV spectrum of 10 showed three bands at 224, 246, and 367 nm, as seen in the spectra of 2-4, and pH-dependent absorptions of the third band were applied in its pK_R^+ measurement (vide infra).





Note that the structure of **13** is unusual; cyclizations of various cycloheptatrienylethanones **15** under the same reaction conditions yielded 1,2,3,8-tetrahydroazulen-1-ones instead of the 1,2,3,3a-isomer **16** (Scheme 2).^[3–5,7] Since the Nazarov cyclization is believed to proceed through a 4π -conrotatory electrocyclization of protonated intermediate **18**,^[10,13] the key process for giving a different product is the deprotonation of oxyallyl cation intermediate **19** (Scheme 3). The unusual formation of **13** (**22**) in this study is rationalized based on density functional theory (DFT) calculations^[14] of possible enol intermediates **20** and **21**, as



Figure 2. Proton chemical shifts [δ , ppm] in CD₃CN of **10** (left) and the result of NOE experiments (right).

Table 1. Chemical shifts [δ , ppm] of the olefinic protons of cations 2, 3, 4, and 10 in CD₃CN.

Entry		H-2	H-3	H-4	H-5	H-6	H-7	H-8
1	2 ^[a]	7.72	7.33	8.96	8.90	8.75	8.77	9.00
2	3 ^[a]	8.13	7.49	9.12	9.00	8.85	9.01	9.10
3	4 ^[a]	8.00	7.42	8.99	8.90	8.74	8.82	9.07
4	10	8.53	7.47	8.94	8.86	8.74	8.74	9.72

[a] Data taken from ref.^[3b].

follows. Calculations at the B3LYP/6-31G(d) level of theory predict that enol **20** is more stable than **21** for the adamantane-connected system, whereas enol **20** is less stable than **21** for the cyclohexane-connected system (Figure 3). The inverted energy difference for the adamatyl system is mainly due to the short atomic distances (192.3 and 211.5 pm) between H-8 and hydrogens on the adamantyl group in **21**. Besides the theoretical study, the approach of either a solvent molecule or its conjugate base for the deprotonation of H-8a in **19** is thought to suffer from steric repulsion with the adjacent methylene protons at the adamantyl group, judging from the Dreiding model study. In fact, congestion around H-8a is also seen in the reaction rate of hydride abstraction from **14**; while the reactions of



Scheme 2. Nazarov cyclization of 15.

1,4-dihydroazulenes with trityl cation were complete within 1 h at room temperature, the reaction of 14 requires 17 h at 55 °C.



Scheme 3. Possible reaction paths for the Nazarov cyclization.



Figure 3. Enol intermediates calculated at the B3LYP/6-31G(d) level of theory. Values in parentheses are relative total energies [kcalmol⁻¹].

Assuming an equilibrium between a carbocation and its corresponding alcohol [Equation (1)], the pK_R^+ value, which indicates thermodynamic stability for the carbocations, can be determined.^[1a]

$$R^{+} + H_2 O \rightleftharpoons ROH + H^{+} \tag{1}$$

The pK_R^+ value of **10** was determined to be 9.8 by the UV method in 50% aqueous acetonitrile solution. The thermodynamic stability of **10** is greater than that of the tropylium cation (**1**),^[6] and is comparable to those of cations **2** and **3**. The reduction potential of carbocations indicates their reluctance for reduction and provides another empirical stability parameter for carbocations.^[15] The reduction potentials for various azulenium ions measured by cyclic voltammetry along with pK_R^+ values are shown in Table 2. The reduction potential of **10** is greater than that of **2** or **3**, and is the same as that of **4**. Both the pK_R^+ value and the reduction potential of **10** are less than that expected

by inductive stabilization of the nine carbons at the 1-position. It is thought to be difficult for the adamantyl group to accumulate the inductive effect because of its intricate structural nature. Additionally, ineffective solvation due to congestion around the carbon atom at the 1-position can also apply to **10**, as was suggested for **9**.^[5] In order to obtain further structural information on the perchlorate salt of **10**, we examined its X-ray crystal structure.

Table 2. pK_R^+ values and reduction potentials of 2–4, 7–9, and 10.

Entry	Cation	pK_R^+ value ^[a]	Reduction potentials (V vs. SCE) ^[b]
1	2 ^[c]	9.9	-0.41
2	3 ^[c]	10.0	-0.46
3	4 [c]	10.4	-0.54
4	7 ^[d]	8.6	-0.38
5	8 ^[d]	10.1	-0.45
6	9 ^[d]	9.2	-0.46
7	10 ^[e]	9.8	-0.54

[a] For measurements, see the Experimental Section. [b] Irreversible. [c] Taken from ref.^[3b]. [d] Taken from ref.^[5]. [e] This study.

Yellowish prismatic crystals of the perchlorate salt of 10 were obtained by recrystallization from a mixture of *n*-hexane and dichloromethane. ORTEP drawings and the crystal packing of 10 are shown in Figure 4. The C-C bond lengths of the azulenyl part are comparable to those of 3 (Figure 5).^[3b] Bond alternation of the seven-membered ring is as small as that of 3. Slightly longer C-C bond lengths (157.2 and 156.7 pm) at the C-1'(C-1) of the adamantyl group imply σ - π conjugation, as seen in 3. The azulenyl part of the crystal structure is non-planar, and the adamantyl group is not symmetric against the azulenyl plane. The deviation of carbons of the azulenyl part from its mean plane is also shown in Figure 5. The average of the deviation is 4.62 pm, which is greater than that of 3 (1.15 and 1.34 pm)^[3b] and 5 (0.41 pm),^[3d,3e] indicating clear deformation of the azulenyl ring. Since the perchlorate salt of 10 has the same atom arrangement on both sides of the azulenyl plane and there is sufficient space for the plane to spread in the crystal cell, as seen in its packing, the deformation of the azulenyl plane can be ascribed neither to the steric congestion between H-2 and Ha and between H-8 and H_b nor to the packing of the azulenyl part in the cell. The distances between perchlorate oxygens and H-2 and H-4 was found to be in the range of 238.1-259.3 pm, which are sufficiently short to suggest CH–O interactions. Thus, the deformation is rather considered to be derived from these interactions, and it is assumed that 10 should have a planar azulenvl part in solution or the gas phase, unlike it does in the crystal structure. Indeed, DFT calculations of cation 10 predict a planar structure (Figure 6), though the structure shows shorter atomic distances between H-2 and H_a and between H-8 and H_b. The X-ray and theoretical structures support the crowding-atom arrangement and the steric compression shift in the ¹H NMR spectrum. The average distances between H_a and H-2 and between H_b and H-8 in the crystal structure are 214.0 and 199.0 pm, respectively.

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238.1 pm

Figure 4. Crystal packing and ORTEP drawings of 10.



Figure 5. Bond lengths [pm] (left) of 10 and deviations [pm] (right) of the azulenyl carbons from its mean plane.



Figure 6. Optimized structure (Chem3D output) of cation 10 and atomic distances [pm]. Values from the for X-ray analysis are shown in parentheses.

Conclusions

We have applied previously developed methodology for azulenium cations to the synthesis of the novel azulenium ion **10**. The Nazarov reaction of aldol-type adduct **12** provided a C–C double bond position isomer **13**, which has never been obtained in similar reactions forming other tetrahydroazulenones. The formation of **13** was discussed based on DFT calculations of enol intermediates. The ¹H NMR spectrum of **10** showed a clear steric compression effect between H_a and H-2 and between H_b and H-8. The pK_R^+ value of **10** was determined to be 9.8, which is less than that expected by inductive stabilization by the number of carbons of the exocyclic rings at the 1-position. The X-ray crystal structure of the perchlorate salt of **10** reveals CH–O interactions and deformation of the azulenium ion part.

Experimental Section

General Remarks: Melting points were measured with a Yanaco MP-3 and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum RX I spectrometer. UV spectra were measured with a Shimadzu UV1600 spectrometer. ¹H and ¹³C NMR were recorded with tetramethylsilane as an internal standard with



a JEOL $\alpha 400$ spectrometer. Mass spectra were measured with a JMS-700 mass spectrometer. Cyclic voltammograms were recorded with a Yanaco P11000 instrument. Column chromatography was performed with Merck Kieselgel 60 Art 7743 or Wako activated alumina. Diethyl ether was purified from sodium and benzophenone by distillation under an argon atmosphere. A diethyl ether solution of methyllithium was purchased from Kanto Chem. Co. and was titrated before use. Trimethylsilyl triflate was purchased from Tokyo Chemical Industry, Inc. The synthesis of **11** was previously reported.^[7] Trityl perchlorate was prepared by the method of Dauben et al.^[16]

1-(Cyclohepta-1,3,5-trienyl)-2-(2-methoxyadamant-2-yl)ethanone (12): A solution of trimethylsilyl triflate (92 µL, 50.0 mmol) in 1 mL of dichloromethane was added dropwise to a solution of silyl enol ether 11 (1.03 g, 5.00 mmol) and 2,2-dimethoxyadamantane^[17] (0.981 g, 5.50 mmol) in dichloromethane (25 mL) at -78 °C under a nitrogen atmosphere. After being stirred for 12 h, the reaction mixture was poured into of ice/water (50 mL). The aqueous layer was extracted with dichloromethane $(2 \times 50 \text{ mL})$. The combined organic layers were washed with saturated aqueous NaHCO₃ and brine and then dried with anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO₂, 3% ethyl acetate in hexane as the eluent) to give 0.659 g (44% yield) of 12 as a pale yellow solid; m.p. 81-82 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.49 (dm, J = 12.0 Hz, 2 H), 1.69 (br. s, 2 H), 1.76-1.79 (m, 3 H), 1.86-1.89 (m, 3 H), 2.11-2.13 (m, 4 H), 2.65 (d, J = 7.1 Hz, 2 H), 3.09 (s, 2 H), 3.16 (s, 3 H), 5.57 (dt, J = 9.2, 7.1 Hz, 1 H), 6.25 (dd, J = 9.2, 5.8 Hz, 1 H), 6.69 (dd, J = 10.9, 6.0 Hz, 1 H), 6.83 (dd, J = 10.9, 5.8 Hz, 1 H), 7.07 (d, J = 6.0 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 26.1, 27.0, 27.4, 32.7, 34.5, 34.6, 38.3, 39.1, 48.4, 80.2, 125.9, 126.9, 129.0, 131.1, 133.7, 135.5, 198.9 ppm. IR (KBr): $\tilde{v} = 2910$ (s), 2860 (m), 1645 (s), 1162 (m) cm⁻¹. MS (70 eV): m/z (%) = 298 (1) [M]⁺, 266 (17), 165 (35), 122 (12), 119 (20), 118 (100), 91 (45), 90 (33). C₂₀H₂₆O₂ (298.4): calcd. C 80.50, H 8.78; found C 80.71, H 8.89.

1',2',3',8a'-Tetrahydrospiro[adamantane-2,1'-azulen]-3'-one (13): A mixture of 12 (400 mg, 1.34 mmol) in formic acid (10 mL) and phosphoric acid (10 mL) was heated at 90 °C for 12 h. The resuling dark brown mixture was then poured into water and was extracted with diethyl ether $(3 \times 50 \text{ mL})$. The combined organic layers were washed with saturated aqueous NaHCO3 and brine and then dried with anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO₂, 3% ethyl acetate in hexane as the eluent) to give 180 mg (50% yield) of 13 as yellow microcrystals; m.p. 117-118 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.54 (m, 1 H), 1.60–1.88 (m, 11 H), 2.08 (dm, J = 13.2 Hz, 1 H), 2.20 (m, 1 H), 2.31 (d, J = 5.2 Hz, 1 H), 2.32 (d, J = 17.6 Hz, 1 H), 2.89 (d, J = 17.6 Hz, 1 H), 5.58 (dt, J = 9.2, 5.2 Hz, 1 H), 6.37 (dd, J = 9.2, 6.0 Hz, 1 H), 6.84 (dd, J= 10.4, 6.0 Hz, 1 H), 6.93 (dd, J = 10.4, 6.0 Hz, 1 H), 6.99 (d, J =6.0 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 26.7, 27.5,$ 33.4, 33.5, 33.6, 33.8, 34.4, 34.5, 38.4, 44.3, 45.8, 49.1, 122.3, 123.6, 126.2, 129.8, 130.4, 135.7, 203.3 ppm. UV (MeOH): $\lambda = 223, 232$ sh, 294, 317 sh, 372 sh nm. IR (KBr): $\tilde{v} = 2909$ (s), 2855 (s), 1701 (s), 1617 (s), 720 (s) cm⁻¹. MS (70 eV): m/z (%) = 266 (12) [M]⁺, 224 (17), 118 (100), 90 (66). C19H22O (266.4): calcd. C 85.67, H 8.32; found C 85.67, H 8.56.

Synthesis of the Tosylhydrazone of 13: A suspension of **13** (100 mg, 0.376 mmol), tosylhydrazide (70 mg, 0.38 mmol), and dry THF (5 mL) was stirred at 50 °C for 96 h. The solids formed were collected by filtration and washed well with diethyl ether to give 137 mg (84% yield) of the tosylhydrazone of **13** as a yellow powder;

m.p. 189–193 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.26$ (m, 1 H), 1.30 (m 1 H), 1.55–2.00 (m, 12 H), 2.09 (m, 2 H), 2.41 (s, 3 H), 3.04 (d, J = 16.8 Hz, 1 H), 5.32 (dd, J = 10.1, 5.2 Hz, 1 H), 6.24 (dd, J = 10.1, 5.2 Hz, 1 H), 6.73 (m, 2 H), 6.88 (d, J = 5.6 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.54 (s, 1 H), 7.85 (d, J = 8.1 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 21.6$, 26.7, 27.4, 33.56, 33.64, 33.85, 33.89 (2 C), 33.96, 34.3, 38.3, 46.7, 47.6, 118.0, 119.8, 125.7, 128.0, 129.6, 130.5, 131.0, 132.1, 135.4, 144.0, 157.5 ppm. IR (KBr): $\tilde{v} = 2909$ (s), 1162 (s) cm⁻¹. MS (70 eV): m/z (%) = 434 (9) [M]⁺, 297 (100), 250 (65), 193 (16), 179 (14), 141 (19), 135 (34), 129 (25), 91 (57). C₂₆H₃₀N₂O₂S (434.6): calcd. C 71.89, H 6.96, N 6.45; found C 71.88, H 7.00, N 6.49.

1',8a'-Dihydrospiro[adamantane-2,1'-azulene] (14): To a suspension of 16 (200 mg, 0.461 mmol) in dry diethyl ether (20 mL) at 0 °C under a nitrogen atmosphere, methyllithium (0.8 M diethyl ether solution, 2.2 mL, 2.3 mmol) was added slowly with a syringe. After the addition, the mixture was stirred for 12 h. The mixture was quenched by adding water carefully and was poured into a mixture of diethyl ether and ice/water. The aqueous layer was extracted with diethyl ether $(2 \times 50 \text{ mL})$. The combined organic layers were washed with brine and dried with anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO₂, hexane as the eluent) to give 13 mg (11% yield) of 14 as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (m, 1 H), 1.56–1.93 (m, 8 H), 1.99 (m, 2 H), 2.09 (tm, J = 10.6 Hz, 2 H), 2.20 (dm, J = 13.2 Hz, 1 H), 2.35 (d, J =5.0 Hz, 1 H, H-8a), 5.10 (dd, J = 9.6, 5.0 Hz, 1 H, H-8), 6.04 (d, J = 5.6 Hz, 1 H, H-2), 6.11 (dd, J = 10.8, 5.6 Hz, 1 H, H-7), 6.14 (d, J = 5.6 Hz, 1 H, H-3), 6.42 (dd, J = 10.8, 5.6 Hz, 1 H, H-6), 6.60 (dd, J = 10.8, 5.6 Hz, 1 H, H-5), 6.68 (d, J = 5.6 Hz, 1 H, H-4)ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 26.8, 27.8, 31.4, 32.5, 33.8, 34.90, 34.92, 38.3, 39.8, 49.0, 56.4, 114.0, 120.1, 124.2, 127.8, 129.1, 130.8, 144.6, 148.8 ppm. UV (MeOH): $\lambda = 229$, 234 sh, 318 nm. IR (KBr): $\tilde{v} = 3050$ (w), 3017 (m), 2908 (vs), 2856 (s), 1623 (m), 1455 (s), 704 (s) cm⁻¹. MS (70 eV): m/z (%) = 250 (100) [M]⁺, 193 (20), 179 (18), 154 (32), 135 (63), 128 (42), 115 (18), 91 (17). HRMS: calcd. for C₁₉H₂₂ [M] 250.1723; found 250.1722.

1'H-Spiro[adamantane-2,1'-azulenium] Perchlorate (10): To a solution of 14 (101 mg, 0.404 mmol) in acetonitrile (5 mL) under a nitrogen atmosphere was added trityl perchlorate (134 mg, 1.00 mmol) in one portion. The mixture was stirred at 55 °C for 17 h. The solvent was removed under reduced pressure, and the residue was dissolved in the least amount of dichloromethane possible. Diethyl ether was added to the solution, and solids formed were collected and washed well with cold diethyl ether to give 90 mg of perchlorate salt of 10 as yellowish brown crystals; m.p. 180 °C (dec.). ¹H NMR (400 MHz, CD₃CN): δ = 1.72 (m, 2 H), 1.92–2.30 (m, 8 H), 2.47 (dm, J = 14.0 Hz, 2 H), 2.72 (dm, J =14.0 Hz, 2 H), 7.47 (d, J = 6.0 Hz, 1 H), 8.53 (d, J = 6.0 Hz, 1 H), 8.74 (m, 2 H), 8.86 (t, J = 10.6 Hz, 1 H), 8.94 (d, J = 10.6 Hz, 1 H), 9.72 (d, J = 10.6 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CD₃CN): $\delta = 27.6, 28.9, 34.6, 35.9, 38.0, 40.5, 66.8, 134.7, 145.2, 147.5, 147.8,$ 149.4, 153.1, 168.7, 171.7, 177.1 ppm. UV (CH₃CN): λ = 224, 246, 280 sh, 367 nm. IR (KBr): v 2917 (s), 1443 (s), 1073 (s) cm⁻¹. MS (70 eV): m/z (%) = 249 (22) $[C_{19}H_{21}]^+$, 248 (100), 205 (19), 193 (11), 191 (52), 179 (24), 165 (23), 152 (12), 141 (10). C₁₉H₂₁ClO₄· 0.2CH₂Cl₂ (365.8): calcd. C 63.04, H 5.90; found C 63.27, H 6.01.

X-ray Crystallographic Analysis of 10: One crystal, having approximate dimensions of $0.40 \times 0.30 \times 0.50$ mm was mounted on a glass fiber. All measurements were conducted with a Rigaku AFC7R diffractometer with graphite monochromated Mo- K_a radiation and a rotating anode generator. Cell constants and an orientation ma-

trix for data collection, obtained from a least-squares refinement with the setting angles of 25 carefully centered reflections in the range $25.45 < 2\theta < 29.46^\circ$, corresponded to a primitive monoclinic cell with dimensions: a = 7.439 (2) Å, b = 17.479 (4) Å, c = 12.878(1) Å, $\beta = 92.52$ (1)°, and V = 1672.9 (4) Å³. For Z = 4 and formula weight: 348.83, the calculated density was 1.38 g cm⁻³. Based on a statistical analysis of the intensity distribution and the successful solution and refinement of the structure, the space group was uniquely determined to be $P2_1/c$ (#14). The data were collected at a temperature of 23 \pm 1 °C with the ω -2 θ scan technique to a maximum 2θ value of 60.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at a halfheight of 0.26° with a take-off angle of 6.0° . Scans of (1.73 + 0.30) $\tan\theta$)° were made at speeds of 8.0° min⁻¹ (in omega). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of 5 scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal-to-detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 5.0 mm (vertical). Of the 5396 reflections collected, 4891 were unique ($R_{int} = 0.028$). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient μ for Mo- K_{α} radiation was 2.5 cm⁻¹. Azimuthal scans of several reflections indicated no need for an absorption correction. The structure was solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix, least-squares refinement was based on 4891 observed reflections [I $> -10.00\sigma(I)$ and 217 variable parameters, and they converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors: R = 0.120, Rw = 0.211, and R1 =0.072 for $I > 2.0\sigma(I)$ data. The standard deviation of an observation of unit weight was 1.05. The weighting scheme was based on counting statistics and included a factor (p = 0.050) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.98 and -0.71 e^{-/} Å³, respectively.

CCDC-677990 (for **10**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Cyclic Voltammetry: A standard three-electrode cell configuration was employed with a glassy carbon disk working electrode, a Pt wire auxiliary electrode, and a Ag wire as an Ag/Ag⁺ quasi-reference electrode. The reference electrode was calibrated at the completion of each measurement on a saturated calomel electrode (SCE). Cyclic voltammetry was measured in acetonitrile solution with tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of 0.1 V s⁻¹ at 25 °C. Under these conditions, ferrocene showed a half-wave oxidation potential of +0.40 V vs. SCE.

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