

Preliminary communication

A stable 6-metallated 1-azafulvene: synthesis and reactions of $\text{Ru}(\text{C}[\text{C}_4\text{H}_3\text{N}]\text{SCNMe}_2\text{S})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)$ and crystal structure of $[\text{Ru}\{\text{=C}(\text{SCNMe}_2\text{S})(2\text{-pyrrolyl})\}(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]^+$

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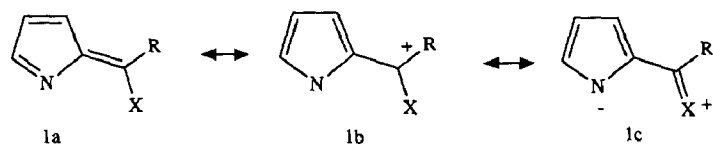
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(Received January 30th, 1990)

Abstract

Dimethyldithiocarbamate displaces chloride from both the carbene centre and the metal in $\text{Ru}[\text{=CCl}(2\text{-pyrrolyl})]\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ to give the stable ruthenium-substituted 1-azafulvene $\text{Ru}(\text{C}[\text{C}_4\text{H}_3\text{N}]\text{SCNMe}_2\text{S})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)$ (A). Compound A can be protonated (reversibly) or methylated at the nitrogen of the 1-azafulvene to give compounds B and C respectively. The structure of B has been determined by a single crystal X-ray study.

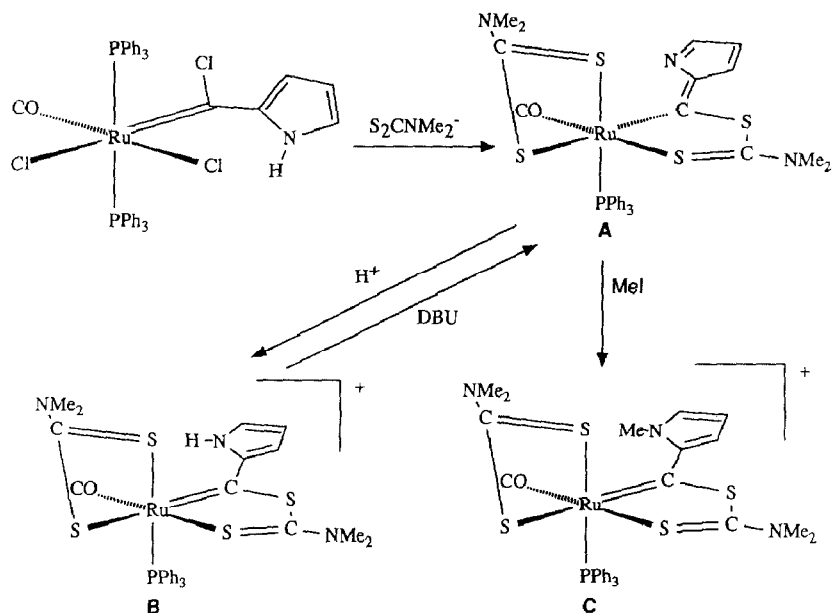
1-Azafulvenes are reactive species of which there are comparatively few stable examples [1]. There is one example of a 1-azafulvene being stabilised by *N*-coordi-



nation to a metal–ligand fragment [2] as in 2. Consideration of canonical form 1c



above suggests that attachment of an electron-releasing metal–ligand fragment at the 6-position of a 1-azafulvene as in 3 should also have a stabilising effect. If the ML_n fragment had bulky ligands then some steric protection of the very electro-



Scheme 1

philic C-6 site might also result. In the preceding communication [4] we described a non-isolable 1-azafulvene metal complex from reaction of a chloropyrrolylcarbene complex of ruthenium with catecholates. Herein we report that replacement of catecholates in the above reaction by the singly charged bidentate ligand, dimethyldithiocarbamate yields a stable 1-azafulvene complex (A), and that the complex A can be protonated (reversibly) and methylated at the 1-azafulvene nitrogen atom. We also report the crystal structure of the protonated derivative $[\text{Ru}\{\text{C}(\text{SCNMe}_2\text{S})(2\text{-pyrrolyl})\}(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]\text{ClO}_4$.

Treatment of $\text{Ru}\{=\text{C}(\text{Cl})(2\text{-pyrrolyl})\}\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ [3] with sodium dimethyldithiocarbamate results in displacement of chloride from both the carbene centre and the metal, with the carbamate ligand bridging the Ru–C bond just as the catecholates group does [4]. However, in the case of carbamate the remaining chloride ligand is also displaced from the metal, together with a triphenylphosphine ligand, and under the reaction conditions the nitrogen atom of the pyrrole ring is deprotonated to yield the uncharged 6-metallated 1-azafulvene complex $\text{Ru}\{\text{C}[\text{C}_4\text{H}_3\text{N}]\text{SCNMe}_2\text{S}\}(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)$ (A). This transformation and the further reactions of A are depicted in Scheme 1. IR, ^1H , and ^{13}C NMR data for compounds A, B, and C are presented in Table 1.

Compound A is readily protonated by addition of acid to give the cation B, and deprotonation of B is brought about by addition of the base DBU. A is also rapidly methylated at room temperature by addition of MeI to form the cation C.

To confirm the proposed metallacycle formulation the crystal structure of cation B, as its perchlorate salt $[\text{Ru}\{\text{C}(\text{C}_4\text{H}_3\text{NH})\text{SCNMe}_2\text{S}\}(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]\text{ClO}_4$, was determined. Crystal data: $\text{C}_{30}\text{H}_{31}\text{ClN}_3\text{O}_5\text{PS}_4\text{Ru}$, $M = 808.98$, monoclinic, space group, $P2_1/c$, a 11.019(1), b 15.242(2), c 20.542(1) Å, β 91.947(6)°, U 3448.2 Å³, $z = 4$, D_c 1.558 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ 8.44 cm⁻¹, 4437 observed data ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at room temperature using

Table 1
IR^a and NMR data^b for ruthenium complexes

Compound ^c	$\nu(\text{CO})$	Other bands	¹ H	¹³ C
(A) Ru(C ₄ H ₃ N)SCNMe ₂ S(η^2 -S ₂ CNMe ₂)CO(PPh ₃) ^d	1948	1518, $\nu(\text{CN})$; 1350, 1259m, 1153m, 1005m, 814m	(6.40, d, 1H, $J = 4.4, 7.63$, 1H), C ₄ H ₃ N	(124.56, 135.16, 151.03, 163.37), C ₄ H ₃ N; 201.28, d, $J = 13.1$, M-C-6-azafulvene; 219.14, d, $J = 9.4$, M-CO
(B) [Ru(=C(2-pyrrolyl)SCNMe ₂ S)(η^2 -S ₂ CNMe ₂)CO(PPh ₃)]ClO ₄ ^e	1969	3250br, $\nu(\text{NH})$; 1533, $\nu(\text{CN})$; 1395, 1333, 1249m, 1152, 1103br, $\nu(\text{ClO}_4)$; 1049, 872w, 810m, 793, 625m	(6.34, m, 1H, 7.16m, 1H, 7.64, 1H), C ₄ H ₃ N; 11.11, br, 1H, NH	(118.19, 136.58, 147.34, q), C ₄ H ₃ N; 199.12, d, q, $J = 11.7$, M-CO; 260.41, d, q, $J = 8.2$, C _{carbene}
(C) Ru(=C(2-N-methylpyrrolyl)CNMe ₂ S)(η^2 -S ₂ CNMe ₂)CO(PPh ₃)ClO ₄	1969	1533, $\nu(\text{CN})$, 1339m, 1314m, 1248m, 1152m, 831w, 812w, 1092br, $\nu(\text{ClO}_4)$; 792w, 623, m	3.82, 3H, C ₄ H ₃ NMe; 6.23, m, 1H, 6.71, d, 1H, $J = 4.0$, C ₄ H ₃ N	39.18, C ₄ H ₃ NMe; (114.30, 131.27, 140.48, 149.13, q), C ₄ H ₃ N; 197.59, d, q, $J = 11.4$, M-CO; 271.76, d, q, $J = 7.2$, C _{carbene}

^a cm⁻¹ measured as Nujol mults. All bands strong unless otherwise noted. ^b δ in ppm, coupling constants in Hz. ^c All compounds have satisfactory C, H and N analyses. ^d one C₄H₃N resonance obscured beneath PPh₃. ^e one C₄H₃N resonance not observed, possibly coincident with another signal.

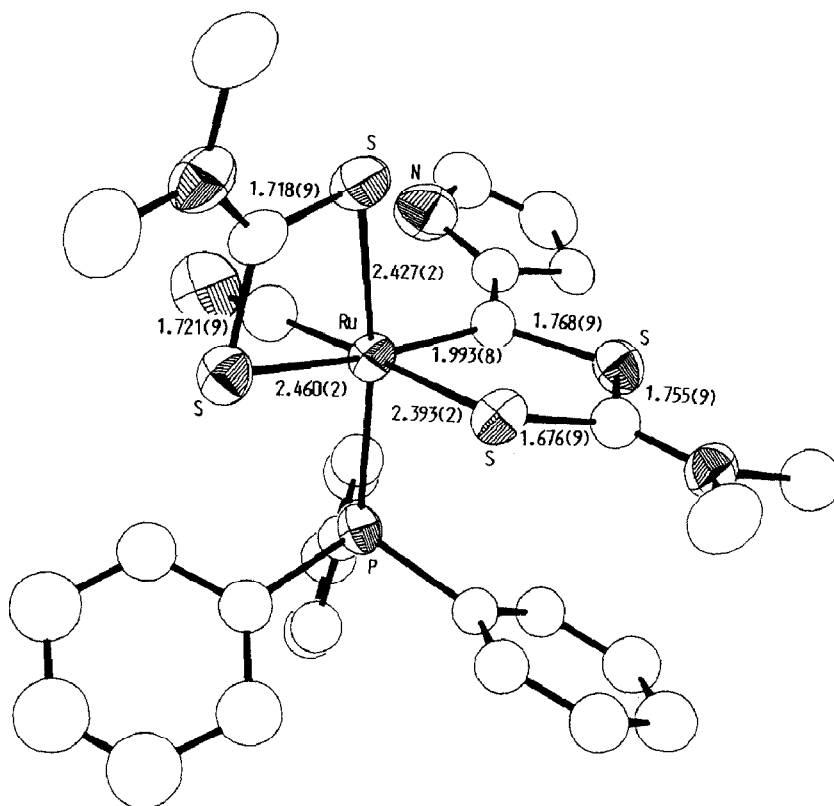
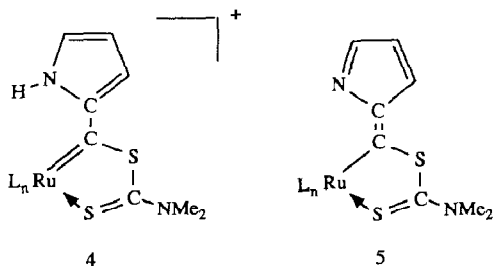


Fig. 1. Molecular structure of $[\text{Ru}(=\text{C}(\text{C}_4\text{H}_3\text{NH})\text{SCNMe}_2\text{S})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]^+$.

Mo- K_α radiation (λ 0.71069 Å). Data were corrected for Lorentz, polarisation, and absorption effects. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares to $R = 0.053$, $R_w = 0.060$. Tables of atom coordinates and bond parameters have been deposited at the Cambridge Crystallographic Data Centre.

The structure is shown in Fig. 1. The observed C-S bond distances are compatible with a representation of the bonding as in 4, and so suggest that the bonding in compound A can be represented as in 5.



References

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