

Journal of Organometallic Chemistry, 387 (1990) C5–C8
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20793PC

Preliminary communication

**Catecholate spanning a metal–carbon double bond.
 Synthesis and crystal structure of $\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})\text{-(2-}N\text{-methylpyrrolyl)]\text{I}(\text{CO})(\text{PPh}_3)_2$**

G.J. Irvine, C.E.F. Rickard, W.R. Roper* and L.J. Wright

Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received January 30th, 1990)

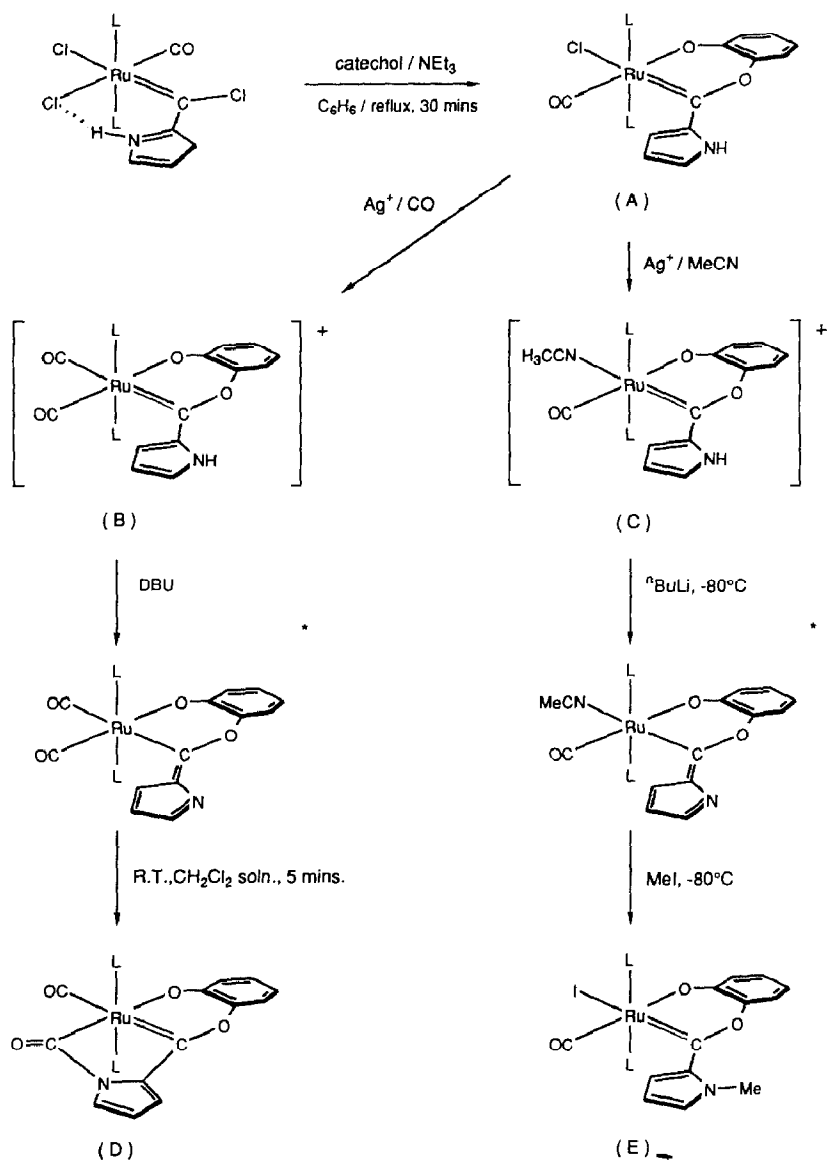
Abstract

Catecholate displaces chloride from both the carbene centre and the metal in $\text{Ru}[\text{=CCl}(2\text{-pyrrolyl})]\text{Cl}_2(\text{CO})\text{L}_2$ ($\text{L} = \text{PPh}_3$) to give $\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})]\text{Cl}(\text{CO})\text{L}_2$ (**A**). Cations derived from **A** can be deprotonated to ruthenium-substituted 1-azafulvene intermediates which undergo further reactions including methylation at nitrogen to give $\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-}N\text{-methylpyrrolyl})]\text{I}(\text{CO})\text{L}_2$ (**E**). The crystal structure of **E** is reported.

We recently reported the synthesis of the chloropyrrolylcarbene complex $\text{Ru}[\text{=CCl}(2\text{-pyrrolyl})]\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ and showed that the chloride on the carbene carbon atom is readily replaced in substitution reactions [1]. Furthermore, the nitrogen atom bears a hydrogen substituent thus allowing further elaboration. Herein we report (i) the synthesis of new ruthenium(II) pyrrolylcarbene complexes where catecholate spans the ruthenium–carbon double bond, (ii) the deprotonation of cationic derivatives of this metallacycle to yield intermediate 1-azafulvene complexes and (iii) intra- and inter-molecular reactions of these intermediate compounds.

Heating under reflux solutions of $\text{Ru}[\text{=CCl}(2\text{-pyrrolyl})]\text{Cl}_2(\text{CO})(\text{PPh}_3)$ and *p*-cresol in benzene in the presence of triethylamine gives the *N*-metallated product $\text{Ru}[\text{=C}(\text{O-}p\text{-tolyl})(\text{C}_4\text{H}_3\text{N})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$, which is clearly related to the *N*-metallated compound previously characterised by a crystal structure determination [1]. In contrast, under similar reaction conditions but with the dihydroxybenzene cathechol, there is chloride displacement from both the carbene centre and the metal, to form **A** (Scheme 1).

For compound **A** a strong $\nu(\text{NH})$ band at 3303 cm^{-1} is evident in the IR spectrum (see Table 1 for IR data for all compounds reported.) The nitrogen atom of the pyrrolyl group in **A** is available for further elaboration. Deprotonation becomes facile if the complex is first converted to a cation. This can be accom-



Scheme 1. L = PPh₃, ★ observable intermediate, not fully characterized.

plished by reaction of **A** either with AgClO₄ in the presence of CO, or with AgSbF₆ in the presence of CH₃CN, to yield $[\text{Ru}=\text{C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})(\text{CO})_2\text{L}_2]^+$ (**B**) and $[\text{Ru}=\text{C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})(\text{CO})(\text{CH}_3\text{CN})\text{L}_2]^+$ (**C**) respectively (Scheme 1).

Addition of the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to a solution of **B** in tetrahydrofuran (THF) at room temperature causes an immediate colour change from red to light green-yellow and then to deep purple during a few minutes. A crystalline solid of the same colour can be isolated from solution upon the addition of ethanol. Unlike **B** this product has only one $\nu(\text{CO})$ band at 1970 cm^{-1} in the IR spectrum and a strong new band at 1663 cm^{-1} . No N-H activity appears in either the IR or ¹H NMR spectra. We formulate the product as the metallabicyclic

Table 1

IR data ^a for ruthenium complexes

Compound ^b	$\nu(\text{CO})$	$\nu(\text{NH})$	Other bands
$\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})]\text{Cl}(\text{CO})\text{L}_2$ (A)	1954	3303m,br	1597m,1333,1323,1262,1218m, 1121,1059m,902m
$[\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})](\text{CO})_2\text{L}_2]\text{ClO}_4$ (B)	2071, 1984	3267w,vbr	1598m,1534m,1418,1356 1330m,1264,1095,1058,902m, 848m,637m
$[\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-pyrrolyl})](\text{MeCN})(\text{CO})\text{L}_2]\text{SbF}_6$ (C)	1971	3400w,br	2072w,1600m,1533w,1417, 1331,1262,1200,1061,905m, 850m,659
$\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(\text{C}_4\text{H}_3\text{NC}(\text{O}))](\text{CO})\text{L}_2$ (D)	1970		1663m,1599m,1518m,1402m, 1369,1325m,1297m,1178m, 1048m,948m,667m
$\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-}N\text{-methylpyrrolyl})]\text{I}(\text{CO})\text{L}_2$ (E)	1942		1594m,1399,1330,1258,1226m, 1109m,1069, 909m

^a cm^{-1} measured as Nujol mulls. All bands strong unless otherwise noted. ^b All compounds have satisfactory C, H and N analyses and give the expected ¹H and ¹³C NMR spectra (L = PPh₃).

complex $\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(\text{C}_4\text{H}_3\text{NC}(\text{O}))](\text{CO})\text{L}_2$ (D), and propose that upon deprotonation, a reactive azafulvene ligand is transiently formed (see Scheme 1). The nucleophilic nitrogen atom of this group then attacks the cis-coordinated carbon monoxide forming a new five-membered metallacyclic ring.

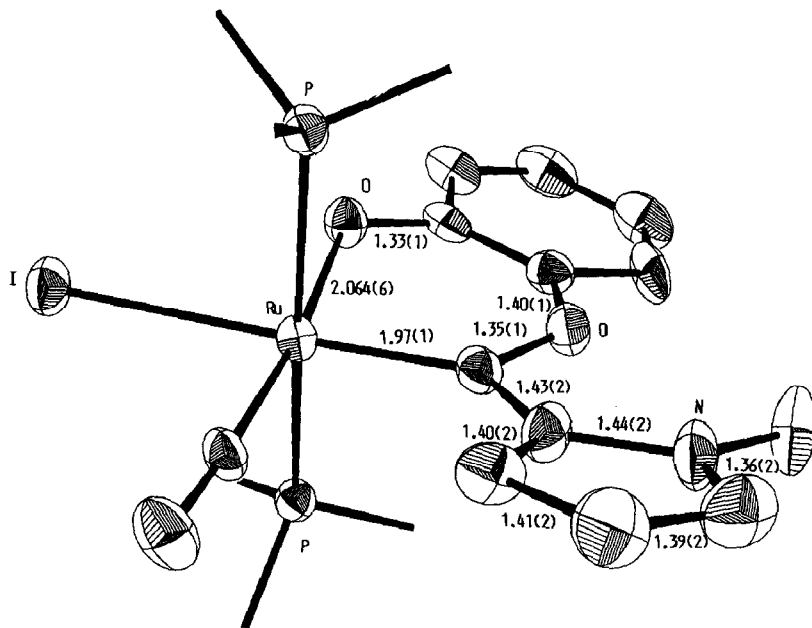


Fig. 1. Molecular structure of $\text{Ru}[\text{=C}(\text{OC}_6\text{H}_4\text{O})(2\text{-}N\text{-methylpyrrolyl})]\text{I}(\text{CO})(\text{PPh}_3)_2$ (phenyl rings omitted for clarity).

The azafulvene intermediate can be trapped at low temperature by reaction with methyl iodide. Thus, treatment of the monocarbonyl cation **C** with ⁿBuLi in THF at -80°C followed by rapid addition of an excess of methyl iodide results in the formation of $\text{Ru}[\text{C}(\text{OC}_6\text{H}_4\text{O})(2\text{-}N\text{-methylpyrrolyl})]\text{I}(\text{CO})\text{L}_2$ (**E**). The structure of **E** was confirmed by a single crystal X-ray study. Suitable single crystals were grown from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. Crystal data: $\text{C}_{49}\text{H}_{40}\text{INO}_3\text{P}_2\text{Ru}$, $M = 980.79$, triclinic, space group $P1$, a 10.769(5), b 10.807(2), c 20.506(2) Å, α 95.64(1), β 87.05(2), γ 117.67(2)°, U 2103.5, $Z = 2$, D_c 1.548 g cm^{-3} , $\mu(\text{Mo-K}\alpha)$ 77.0 cm^{-1} . 3943 observed data ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at room temperature using Mo- $K\alpha$ radiation (λ 0.71069 Å). Data were corrected for Lorentz, polarisation and absorption effects. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares to $R = 0.054$ ($R_w = 0.055$). Tables of atom coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

The structure is shown in Fig. 1 confirming the metallacycle formulation for compounds **A–E**. The Ru–C double bond distance of 1.97(1) Å is typical of values determined previously in related compounds [1]. The catecholate ring lies close to the plane defined by Ru and the 4 donor atoms I, C(CO), C(carbene), O(catecholate). The pyrrole ring is only slightly tilted out of this plane.

1-Azafulvene is a rare ligand in organometallic chemistry. A substituted 1-azafulvene, nitrogen-coordinated to $\text{W}(\text{CO})_5$, has been reported from the reaction between an intermediate metal-ketenimine complex and an alkenyl isocyanide [2]. The possibility of stabilising these reactive molecules through metal complexation (through carbon rather than nitrogen) warrants further investigation.

References

- 1 G.R. Clark, D.J. Hodgson, M.M.P. Ng, C.E.F. Rickard, W.R. Roper, and L.J. Wright, *J. Chem. Soc. Chem. Commun.*, (1988) 1552.
- 2 R. Aumann, E. Kuckert, C. Kruger, and K. Angermund, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 563.