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Preliminary Communication

Insertion of diphenylacetylene into the carbon–sulfur bond of phenylisothiocyanate at a diruthenium centre: synthesis and X-ray structure of $[Cp_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}SC(Ph)=C(Ph)C(=NPh)\}]$

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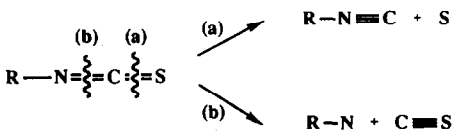
Abstract

Heating a toluene solution of $[Cp_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(Ph)=C(Ph)\}]$, **1**, with phenylisothiocyanate affords $[Cp_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}SC(Ph)=C(Ph)C(=NPh)\}]$, **2**, as a result of alkyne insertion into the carbon–sulfur bond of the isothiocyanate.

Whereas the reactivity of isocyanates with transition metal centres has been studied in some detail [1], reactions of organometallic complexes with the related isothiocyanates have received surprisingly little attention [2]. The latter are, however, potentially useful reagents for introducing a number of ligands to a metal centre. Thus cleavage of the carbon–sulfur bond results in the generation of sulfido and isocyanide moieties, while carbon–nitrogen bond scission leads to the formation of imido and thiocarbonyl ligands. The latter process dominates the chemistry of isocyanates, since the carbon–oxygen double bond is strong and thus not susceptible to scission [3]. In contrast, because of the poorer orbital overlap between carbon and sulfur, the cleavage of this bond is expected to be quite facile in isothiocyanates. Recently we have embarked upon a programme of investigation of the reactivity of isothiocyanates at a variety of metal centres. At high valent metal centres, nitrogen–carbon bond cleavage predominates as a result of the generation of the strong π-donor imido ligand [4]. In contrast, at low valent metal centres we find that cleavage of the carbon–sulfur bond dominates the reactivity. Herein we describe initial studies on the reactivity of phenylisothiocyanate at the acyl stabilised diruthenium centre.



Thermolysis of a toluene solution of $[Cp_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(Ph)=C(Ph)\}]$, **1** [5], with phenylisothiocyanate led to the isolation after chromatography of the new complex $[Cp_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}SC(Ph)=C(Ph)C(=NPh)\}]$, **2**, in 40% yield. Characterisation was made on the basis of the spectroscopic and analytical data [6*]. In order to define the precise nature of isothiocyanate addition, an X-ray crystal structure was carried out, and the results are shown in Fig. 1 [7*]. The molecule consists of two ruthenium atoms 2.777(2) Å apart, each bound to a cyclopentadienyl ligand; the two such ligands are in a mutually *cis* configuration. One ruthenium atom, Ru(1), carries a terminal carbonyl, while a second carbonyl bridges the ruthenium–ruthenium vector asymmetrically [Ru(1)–C(1) 2.247(3), Ru(2)–C(1) 1.927(3) Å]. Also bridging the metal–metal bond is the new ligand formed via the insertion of diphenylacetylene into the carbon–sulfur bond of phenylisothiocyanate. Thus the sulfur bridges the metal–metal vector, again somewhat asymmetrically [Ru(1)–S(1) 2.336(2), Ru(2)–S(1) 2.279(2) Å], and is now bound to one carbon of the diphenylacetylene moiety [S(1)–C(5) 1.797(4) Å]. The carbon–carbon bond length of 1.349(4) Å between the two acetylenic carbons is indicative of the retention of double-bond character. The second carbon of the acetylenic unit is linked to the remainder of the isothiocyanate through a new carbon–carbon bond [C(3)–C(4) 1.518(5) Å], which is also linked through C(4) to ruthenium [Ru(2)–C(3) 2.110(4) Å]. Thus the isocyanide formed from the cleavage reaction appears to have inserted into a ruthenium–carbon bond to generate an iminoacyl fragment: The imine nature is clearly shown by the relatively short carbon–nitrogen distance [N(1)–C(3) 1.288(4) Å], and the bond angle at nitrogen [C(3)–N(1)–C(30) 125.0(3)°].

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* Reference number with asterisk indicates a note in the list of references.

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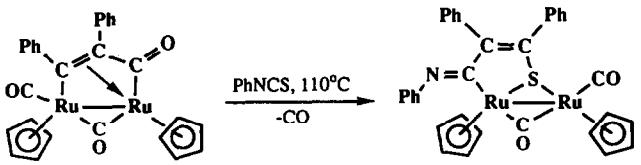

(1) (2)

Overall the formation of **2** involves the cleavage of the carbon–sulfur bond of the isothiocyanate, extrusion of a carbonyl from the acyl unit in **1**, and insertion of both of the cleaved fragments into ruthenium–carbon bonds. The retention of the diphenylacetylene ligand is surprising in view of the number of reactions of **1** previously reported to proceed via alkyne loss [8]. We initially felt that the alkyne was being lost from **1**, and later reinserted into the metal bound isothiocyanate. When the reaction was carried out in the presence of a large excess of cyclopentadienyl monomer (in order to trap released alkyne) a similar yield of **2** was obtained and no trapped species were isolated. It appears that the alkyne is not lost from the diruthenium centre, and indeed, Knox and coworkers have recently noted this in reactions of **1** with isocyanides [9]. While the precise nature of the reaction is as yet unknown, its course differs from that taken by isocyanates. Heating a toluene solution of **1** and phenylisocyanate resulted in a rapid reaction, but the only isolated product was the tetracarbonyl $[CpRu(CO)(\mu\text{-}CO)]_2$ in 76% yield. It is tempting to suggest that the extra carbonyl required for this transformation is derived from the isocyanate, and in support of initial adduct formation is the observation that **1** is stable in refluxing toluene in the absence of other reagents.

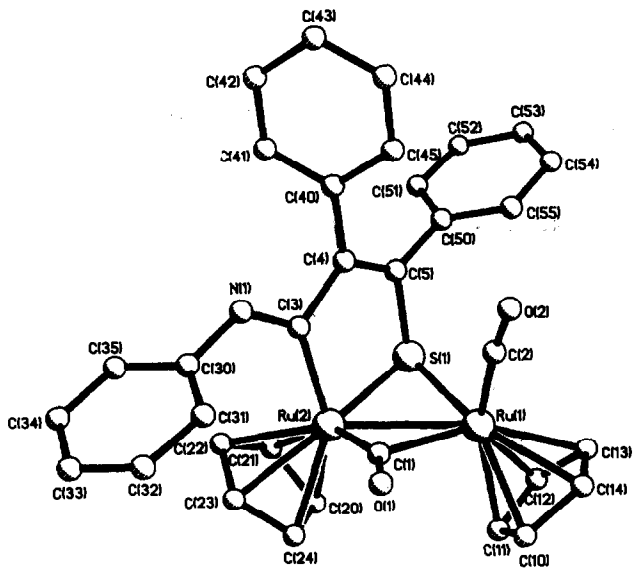

Fig. 1. Molecular structure of $[Cp_2Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}SC(Ph)=C(Ph)C=NPh)]$ **2**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.777(2), Ru(1)–S(1) 2.336(2), Ru(2)–S(1) 2.279(2), Ru(1)–C(1) 2.247(3), Ru(2)–C(1) 1.927(3), Ru(1)–C(2) 1.878(4), C(3)–N(1) 1.288(4), C(4)–C(5) 1.349(4), C(3)–C(4) 1.518(5), Ru(2)–C(3) 2.110(4), Ru(1)–S(1)–Ru(2) 74.0(1), C(3)–N(1)–C(30) 125.0(3).

Two minor products can also be isolated from the reaction of **1** with phenylisothiocyanate, and although we have not as yet fully characterised these, both contain the units of the isothiocyanate and alkyne. We are currently investigating the scope of this reaction towards a range of isothiocyanates and studying the reactivity of **2**. Thus initial results show that the imine moiety, while being susceptible to protonation, is remarkably stable to hydrolysis under neutral and acidic conditions.

References and notes

1 P. Braunstein and D. Nobel, *Chem. Rev., 89* (1989) 1927.
2 See for example: J.D. Wilkins, *J. Organomet. Chem., 65* (1974) 383; R.D. Adams, Z. Dawoodi, D.F. Foust and B.E. Segmuller, *Organometallics, 2* (1983) 315; D. Seyferth, G.B. Womack, C.M. Archer, J.P. Fackler Jr. and D.O. Marler, *Organometallics, 8* (1989) 443; G.R. Lee and N.J. Cooper, *Organometallics, 8* (1989) 1538; V. Crocq, J-C. Daran and Y. Jeannin, *J. Organomet. Chem., 373* (1989) 85.
3 See for example: M.L.H. Green, G. Hogarth, P.C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, (1990) 3781; J.T. Anhaus, T.P. Kee, M.H. Schofield and R.R. Schrock, *J. Am. Chem. Soc., 112* (1990) 1642.
4 G.D. Forster, G. Hogarth and S.P. Redmond, unpublished results.
5 A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, *J. Chem. Soc., Dalton Trans.*, (1982) 1297.
6 Spectroscopic data for **2**: ^1H NMR ($CDCl_3$) δ 7.28–6.76 (m, 15H, Ph), 5.09 (s, 5H, Cp), 4.98 (s, 5H, Cp); ^{13}C NMR ($CDCl_3$) 224.5 (s, μ-CO), 201.2 (s, CO), 130–122 (m, Ph), 121.0 (s, CPh), 119.6 (s, CPh), 87.5 (s, Cp), 84.9 (s, Cp); IR (CH_2Cl_2) 1966s (CO), 1822s (μ-CO), 1605s (C=N), 1548s (C=C) cm^{-1}; MS (m/z) 701 (M^+). Satisfactory elemental analyses were obtained.
7 Structural data for **2**: $Ru_2S_1O_2N_1C_{33}H_{25}$, $M = 669.74$, triclinic, space group $P\bar{1}$, $a = 9.243(5)$, $b = 12.453(4)$, $c = 13.189(7)$ Å, $\alpha = 73.15(3)$, $\beta = 76.48(4)$, $\gamma = 83.27(4)°$, $U = 1410.6(1.1)$ Å^3, $Z = 2$, $T = 292$ K, $D_c = 1.65$ g cm^{-3}, $F(000) = 700$, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 11.51 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.62×0.38×0.22 mm mounted on a Nicolet R3mV diffractometer, by the $\bar{\omega}$–2θ scan technique ($5 \leq 2\theta \leq 50$). From 5241 measured data, 4612 with $I \geq 3\sigma(I)$ were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares to R and R_w values of 0.030 and 0.035. We have also characterised a monoclinic polymorph of **2**. Space group $P2_1/a$, $a = 18.407(9)$, $b = 7.795(5)$, $c = 19.852(10)$ Å, $\beta = 98.33(4)°$. No significant differences in bond length and angles were bound [Ru(1)–Ru(2) 2.783(2), Ru(1)–S(1) 2.327(3), Ru(2)–S(1) 2.295(3) Å].
Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.
8 D.L. Davies, A.F. Dyke, S.A.R. Knox and M.J. Morris, *J. Organomet. Chem., 215* (1981) C30.
9 S.A.R. Knox, personal communication.