Journal of Organometallic Chemistry, 480 (1994) C4–C6

Preliminary Communication

Preparation and structure of a ruthenium dicarbonyl derivative of the $P_2N_4S_2$ ring

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(Received February 22, 1994; in revised form March 31, 1994)

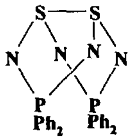
Abstract

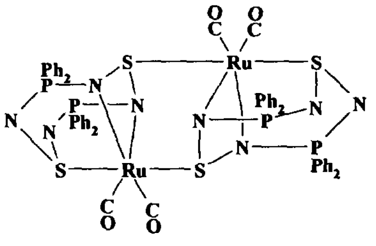
The reaction of $Ru(CO)_4(C_2H_4)$ or $Ru(CO)_5$ with 1,5-$Ph_4P_2N_4S_2$ in CH_2Cl_2/hexane at 23°C produces the dimer $[Ru(CO)_2(Ph_4P_2N_4S_2)]_2$ (2), which was shown by X-ray crystallography to have a centrosymmetric structure in which the $P_2N_4S_2$ ring is attached to one ruthenium atom through two (geminal) nitrogen atoms and the remote sulfur atom and serves as a bridge to the other ruthenium atom via the second sulfur atom. Crystals of $2 \cdot 2(CH_2Cl_2)$ are triclinic, space group $P\bar{1}$ (No. 2), $a = 12.901(1)$ Å, $b = 13.072(1)$ Å, $c = 10.123(1)$ Å, $\alpha = 100.88(1)°$, $\beta = 98.90(1)°$, $\gamma = 67.50(1)°$, $V = 1542.4(3)$ Å^3, $Z = 1$ with final R and R_w values of 0.040 and 0.027, respectively.

Key words: Ruthenium; Sulfur; Nitrogen; Carbonyl

Although nitrogen-containing inorganic heterocycles are potentially versatile ligands for metal carbonyls, very few such complexes have been structurally characterized. A classic example is the half-sandwich π-complex $(\eta^6\text{-}Et_6B_3N_3)Cr(CO)_3$ [1]. The compound $(Me_8P_4N_4)Mo(CO)_3$ has been isolated, but the mode of attachment of the eight-membered ring to the metal is unclear [2]. The formation of explosive, insoluble compounds of unknown structure such as (S_5N_5) Mo(CO) [3], (S_4N_4)Fe(CO) [4] and $S_4N_4Co_2$(CO) [4] from reactions of S_4N_4 with metal carbonyls was reported more than 20 years ago. Subsequently, Herberhold et al. showed that nitrosylation of the latter complex yields $Co(NO)_2(S_3N)$ containing an almost planar CoSSNS ring [5].

Our recent investigations of the ligand behavior of 1, a hybrid of S_4N_4 and $Ph_8P_4N_4$, have shown that the $P_2N_4S_2$ ring is invariably retained in metal complexes [6]. As part of a study of the generality of the displacement of an η^2-alkene in metal complexes by the bidentate (η^2-S, S') $P_2N_4S_2$ ligand [6a], we report here that the reaction between 1 and $Ru(CO)_4(C_2H_4)$ produces $[Ru(CO)_2(Ph_4P_2N_4S_2)]_2$ (2), the first metal carbonyl derivative of this inorganic heterocycle.





The reaction between 1 and $Ru(CO)_4(C_2H_4)$ in dichloromethane/hexane at room temperature produces a yellow solution from which complex 2 was isolated in 54% yield [7]. The same product was obtained in 11% yield from 1 and $Ru(CO)_5$ under similar conditions.

The analytical data for 2 indicate that the heterocyclic ligand has displaced ethylene and two CO ligands (or three CO ligands in the case of $Ru(CO)_5$). The FAB mass spectrum reveals a dimeric molecule as the parent ion and the sequential loss of four CO ligands. The ^{31}P NMR spectrum of 2 shows a singlet at 63.9 ppm suggesting that the $P_2N_4S_2$ ring is bonded symmetrically to the ruthenium centres and that the transannular S–S interaction in 1 has been disrupted [6c]. The ^{13}C NMR spectrum of 2 shows a singlet at 193.7 ppm (in addition to the C_6H_5 resonances) demonstrating that all four CO ligands are in equivalent environments. Finally, the IR spectrum of 2 exhibits two bands in the CO stretching region 2040 and 1986 cm^{-1} consistent with a *cis* arrangement for each pair of CO ligands on Ru^{II} centres. The reaction of 1 with $Fe(CO)_5$ in the presence of Me_3NO in THF at 23°C yields a complex with $\delta(^{31}P) = 66$ ppm, possibly $[Fe(CO)_2Ph_4P_2N_4S_2]_2$, which could not be isolated as a pure compound.

In order to determine the mode of attachment of the $P_2N_4S_2$ ring to the $Ru(CO)_2$ groups, an X-ray crystallographic study of $2 \cdot 2(CH_2Cl_2)$ was carried out

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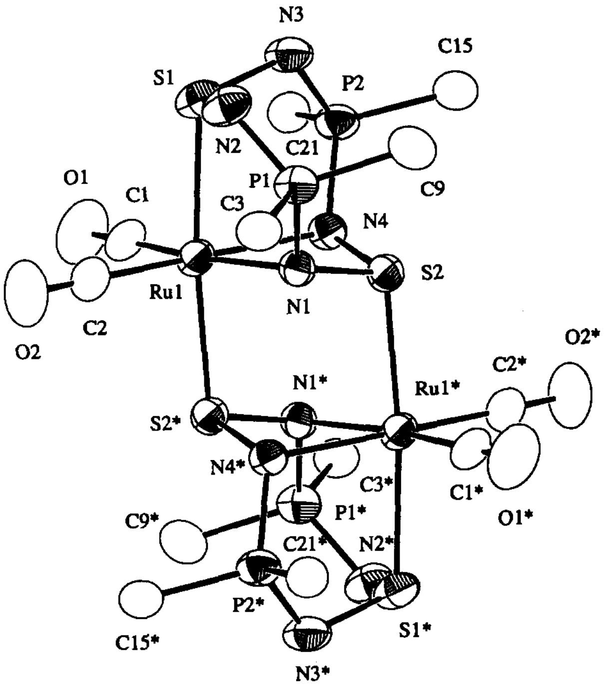

Fig. 1. ORTEP diagram (50% probability ellipsoids) for **2**. For clarity only the α-carbon atoms of C_6H_5 groups attached to phosphorus are shown; selected bond lengths (Å) and angles (°): Ru(1)–S(1) 2.434(2), Ru(1)–S(2)* 2.397(2), Ru(1)–N(1) 2.153(4), Ru(1)–N(4) 2.151(4), Ru(1)–C(1) 1.884(6), Ru(1)–C(2) 1.880(6), N(1)–Ru(1)–N(4) 72.4(1), C(1)–Ru(1)–C(2) 90.1(2), S(1)–Ru(1)–S(2)* 172.96(5). Asterisks indicate symmetry-related atoms.

[10]. As indicated in Fig. 1, the molecule is a centrosymmetric dimer. The heterocyclic ring exhibits an unprecedented tetradentate bonding mode [6] in which it is attached to one ruthenium through two (geminal) nitrogens and the remote sulfur atom and serves as a bridge to the other ruthenium via the second sulfur atom. As a result the $P_2N_4S_2$ ring adopts a chair conformation. The geometry about ruthenium is distorted octahedral with the largest distortion being N(1)–Ru(1)–N(4) = 72.4(1)°. The reasons for this small chelate bite angle are not obvious, but it results in a significantly smaller endocyclic NSN bond angle at S(2) (96.4(2)°) compared to that at S(1) (107.5(2)°). The Ru–N distances are essentially equal at 2.151(4) and 2.153(4) Å and these values are typical for Ru^{II}–N bonds [11]. The S(1)–Ru(1)–S(2)* arrangement is almost linear (172.96(6)°) and the Ru–S distances are normal for ruthenium(II) [11] with that involving the bridging sulfur atom S(2) being shorter than Ru(1)–S(1) (2.434(4) Å). The Ru–Ru distance is 3.94 Å.

In summary, the preparation and structural characterization of **2** demonstrates that the hybrid ring system **1** is a robust and potentially versatile ligand for metal carbonyls.

Supplementary material available. Tables listing atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances, bond angles, anisotropic thermal parameters, and parameters for H atoms have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

This work received financial support from the NSERC (Canada). Helpful advice from Professor J. Takats and Professor W.A.G. Graham is gratefully acknowledged.

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7 A colorless solution of $[Ru(CO)_4(CH_2{=}CH_2)]$ (0.148 g, 0.61 mmol) in deoxygenated hexane (30 ml) was added by cannula (10 min) to a stirred solution of 1,5-$Ph_4P_2N_4S_2$ (0.299 g, 0.61 mmol) in dichloromethane (80 ml) under a nitrogen atmosphere at 23°C. A yellow solution was formed and after 16 h solvent was removed under vacuum to give a yellow-brown product, which was washed with diethyl ether (2×10 ml) and vacuum-dried for 2 h. Recrystallization from dichloromethane/hexane (1:1) gave yellow crystals of **2** (0.213 g, 0.164 mmol, 54%). Anal. Calcd. for $C_{52}H_{40}N_8O_8P_4Ru_2S_4$: C, 48.21; H, 3.11; N, 8.65; S, 9.90. Found: C, 48.09; H, 3.25; N, 8.53; S, 9.79. IR (CH_2Cl_2 solution): $\bar{\nu}$ (cm^{-1}) = 2040, 1986 [ν(CO)]. $^{31}P\{^1H\}$ NMR (23°C, 161.978 MHz, CD_2Cl_2): $\delta = 63.9$(s). ^1H NMR (23°C), 400 MHz, CD_2Cl_2): $\delta =$ 7.15–7.80 (m). ^{13}C NMR (23°C, 75.469 MHz, CD_2Cl_2): $\delta =$ 127.82–135.19 (m, C_6H_5), 193.69 (s, CO). MS (FAB): m/z 1301 ($M+H^+$, 92%), 1273 ($M-CO+H^+$, 36%), 1245 ($M-2CO+H^+$, 44%), 1217 ($M-3CO+H^+$, 34%), 1189 ($M-4CO+H^+$, 100%).

8 Hydrocarbon solutions of $Ru(CO)_4(C_2H_4)$ were prepared by a slight modification of the published procedure [9] involving external photolysis ($\lambda \geq 370$ nm) of $Ru_3(CO)_{12}$ under an atmosphere of ethylene. J. Takats and K. Hoffman, unpublished results.

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10 Suitable crystals (0.50×0.40×0.10 mm^3) of **2**·**2** (CH_2Cl_2) were obtained by the slow diffusion of diethyl ether into a solution of **2** in dichloromethane at 23°C. Crystal data: $C_{54}H_{44}O_4N_8S_4P_4Ru_2Cl_4$, $M = 1465.08$, triclinic, space group $P\bar{1}$ (No. 2), $a =$

12.901(1), $b = 13.072(1)$, $c = 10.123(1)$ Å, $\alpha = 100.88(1)$, $\beta = 98.90(1)$, $\gamma = 67.50(1)^\circ$, $V = 1542.4(3)$ Å^3, $Z = 1$, $\rho_{\text{calc}} = 1.577$ mg m^{-3}, $F(000) = 1472$, $\lambda = 0.71069$ Å, $T = 296$ K, $\mu(\text{Mo K}\alpha) = 0.952$ mm^{-1}. Data were collected on a Rigaku AFC6S diffractometer using the $\omega - 2\theta$ scan technique to a maximum 2θ value to 50.1°. Of a total of 5717 collected reflections, 5452 were unique and corrected for absorption with semi-empirical methods. The structure was solved by the heavy-atom method (SAPI91, Fan Hai-Fu, Structure Analysis Programs with Intelligent Control, Rigaku Corp., Tokyo, Japan, 1991) and refined by full-matrix least-squares on Fs based on 3713 observed reflections [$I > 3.00\ \sigma(\mathrm{I})$]; $R = 0.040$; $R_W = 0.027$; the maximum and minimum peaks in the final difference Fourier map corresponded to 1.44 and -1.10 e Å^{-3}, respectively.

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