

Note

Preparation and molecular structure of a pyrazolyl–ruthenium complex, $\text{Ru}\{\text{C}_3\text{H}_2\text{NN}(\text{SO}_2\text{tol})\}(\text{dppe})\text{Cp}^*$

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Abstract

The reaction between $\text{RuCl}(\text{dppe})\text{Cp}^*$ and $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{SiMe}_3)=\text{NNHTs}$ has given the pyrazole derivative $\text{Ru}(\text{C}=\text{CHNTsN}=\text{CH})(\text{dppe})\text{Cp}^*$ (**1**), which was characterised by a single-crystal X-ray structure determination. Complex **1** is probably formed by attack of the NTs group on the π -complexed desilylated alkyne, with concomitant loss of a proton.
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1. Introduction

Cyclo-addition of 1,3-dipolar molecules to alkynes is an important route to heterocyclic molecules [1]. Thus, azido compounds react with alkynes to give triazoles [2]. Extension to metal azides has given metal-carbon bonded triazolates, although such reactions usually require forcing conditions. Recent accounts of the cyclo-addition of $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}$ with alkynes such as $\text{HC}\equiv\text{CO}_2\text{Me}$ or $\text{C}_2(\text{CO}_2\text{Me})_2$ to give triazolates $\text{Ru}\{\text{N}_3\text{CRC}(\text{CO}_2\text{Me})\}(\text{dppe})\text{Cp}$ ($\text{R} = \text{H}, \text{CO}_2\text{Me}$, respectively) [3] and, more recently, sequential reactions between $\text{M}(\text{CO})_5(\text{CH}_2\text{Cl}_2)$ ($\text{M} = \text{Cr}, \text{W}$), 1-alkynes and diazoalkanes to give 3*H*-pyrazole complexes [4], prompt us to report on the related reaction between $\text{RuCl}(\text{dppe})\text{Cp}^*$ and the alkynyl-(tosyl)hydrazone $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{SiMe}_3)=\text{NNHTs}$.

2. Results

The reaction between $\text{RuCl}(\text{dppe})\text{Cp}^*$ and $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{SiMe}_3)=\text{NNHTs}$ was carried out in methanol in

the presence of KF to induce the proto-desilylation reaction. After heating at reflux point for 3 h, separation of the major product by column chromatography on silica gel afforded yellow crystalline $\text{Ru}(\text{C}=\text{CHNTsN}=\text{CH})(\text{dppe})\text{Cp}^*$ (**1**) in only moderate yield. Elemental microanalyses and electrospray mass spectrometry (ES-MS) showed that the anticipated loss of the tosylhydrazone group had not occurred, the composition being that of the 1/1 adduct of the desilylated precursor and the $\text{Ru}(\text{dppe})\text{Cp}^*$ fragment. The structure portrayed in Fig. 1 was determined from a single crystal X-ray determination and showed that cyclisation to a C-bonded *N*-tosylpyrazolate had occurred (Scheme 1).

The spectroscopic properties of **1** are in accord with the solid-state structure. The IR spectrum contains a single $\nu(\text{C}=\text{C})$ band at 1714 cm^{-1} . The ^1H NMR spectrum contains resonances at δ 1.44 (C_5Me_5), 2.04 and 2.34 (dppe CH_2) and between 7.09–7.57 (aromatic), with two pyrazole ring protons as singlets at δ 6.30 and 6.33; the latter cannot be individually assigned. The aromatic protons of the Ts group were found as a pair of doublets at δ 7.41 and 7.56, while the Me group gives a singlet at δ 2.37. Apart from Cp^* [δ 10.87 (Me), 93.01 (ring C)], dppe carbons [δ 28.50 (CH_2), and between δ 128.27 and 140.83 (Ph)] and Ts groups [δ 21.59

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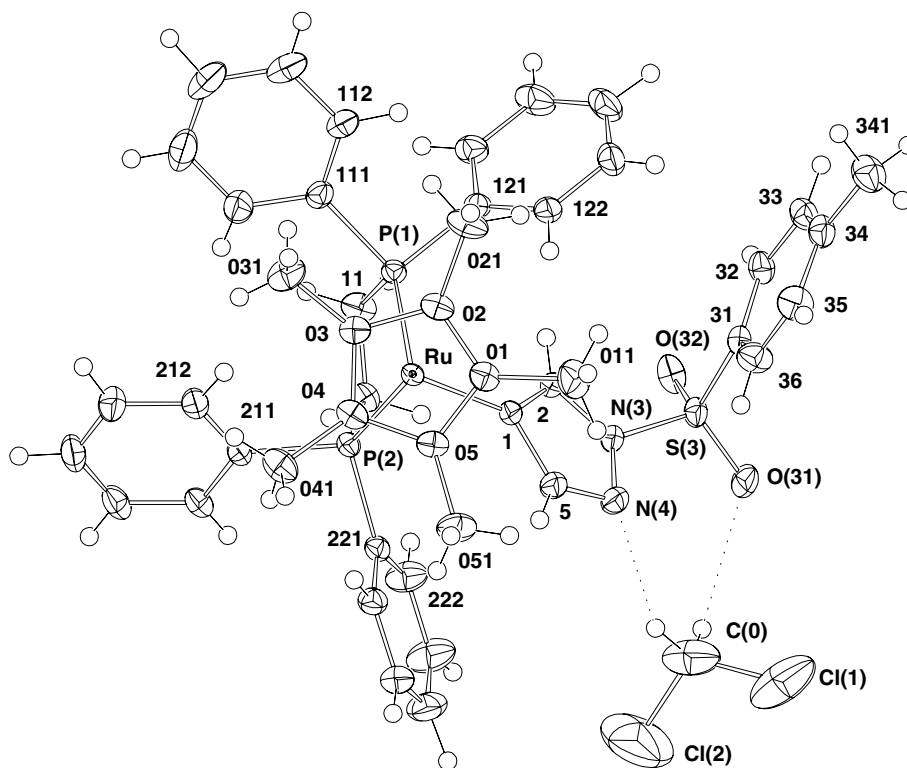


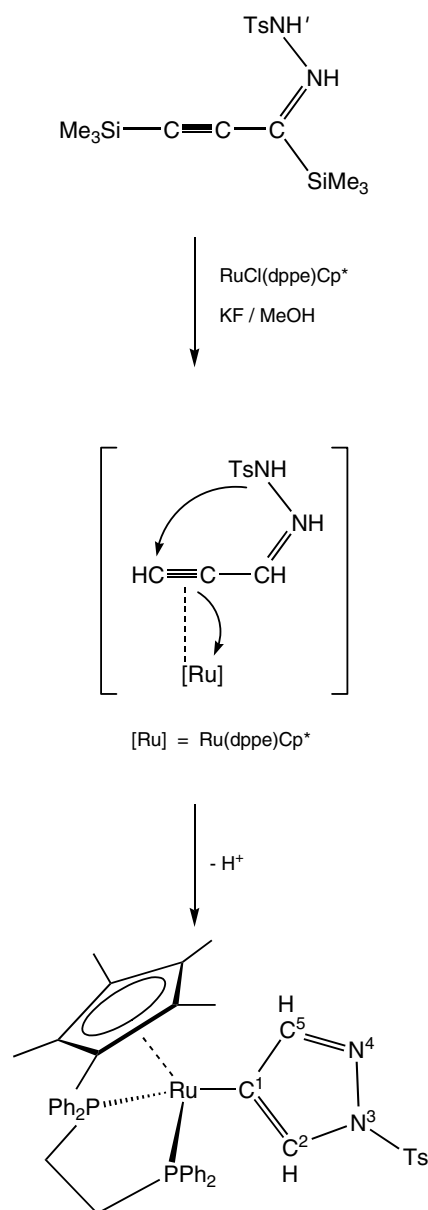
Fig. 1. Plot of a molecule of $\text{Ru}(\text{C}=\text{CHNTsN}=\text{CH})(\text{dppe})\text{Cp}^*$ (**1**). Selected bond distances and angles: Ru–P(1, 2) 2.2690(4), 2.2561(5); Ru–C(1) 2.094(1); C(1)–C(2,5) 1.373(2), 1.445(2); C(2)–N(3) 1.397(2), N(3)–N(4) 1.381(2); N(3)–S(3) 1.665(1); N(4)–C(5) 1.320(2); S(3)–O(31,32) 1.423, 1.431(1) Å. P(1)–Ru–P(2) 83.34(2); P(1, 2)–Ru–C(1) 90.29(4), 80.66(5); Ru–C(1)–C(2,5) 135.8, 123.4(1)°.

(Me), 128.21, 130.25, 137.38, 144.99 (C_6H_4) in the ^{13}C NMR spectrum, only one ring carbon was found at δ 160.13. A 2D NMR HMQC experiment confirms that this resonance interacts with the ^1H resonance at δ 6.33, while the proton at δ_{H} 6.30 is coupled with the resonance at δ_{C} 137.38, suggesting that one of the pyrazole carbons is coincident with this tosyl aromatic signal. The resonance of C(1) was not observed; the other ring carbon resonance is probably also in this region. The dppe ^{31}P nuclei resonate at δ 86.32, while the ES-MS contains $[\text{M} + \text{H}]^+$ and $[\text{M} - \text{Ts}]^+$ at m/z 857 and 701, respectively. In the CV, a single reversible 1-electron oxidation process is found at $E^\circ = 0.27$ V.

The structure of **1** consists of a simple complex formed by coordination of the *N*-tosylpyrazolate group to the $\text{Ru}(\text{dppe})\text{Cp}^*$ fragment. The geometrical parameters of the latter are similar to many other examples reported earlier, with Ru–P 2.2690(4), 2.2561(5) Å and Ru–C(cp*) ranging between 2.265 and 2.273(2) Å (av. 2.26₈ Å). Angles at Ru are consistent with the usual distorted octahedral coordination usually found in these complexes [P(1)–Ru–P(2) 83.34(2), P(1,2)–Ru–C(1) 90.29, 80.66(5)°]. The Cp* methyl carbons lie out of the C_5 -ring plane ($\chi^2 = 4$) by 0.143–0.345(4) Å away from the Ru atom. The most displaced atom is C(051), possibly as a result of the close H(051b)···H(226) separation [2.19(4) Å].

The planar five-membered C_3N_2 ring ($\chi^2 = 372$) is attached to the Ru atom by C(1) [2.094(1) Å] via a normal Ru–C single bond, while the tosyl group remains attached to N(3). Interatomic distances (see Figure caption) are consistent with substantial double bond localisation between C(1)–C(2) [1.373(2) Å] and N(4)–C(5) [1.320(2) Å] and single bonds between C(2)–N(3) [1.397(2) Å] and C(1)–C(5) [1.445(2) Å]. Atom S(3) lies out of the C_3N_2 plane by 0.605(3) Å, consistent with the expected sp^3 hybridisation of N(3), although the sum of angles about this atom (352.0°) suggests that there is considerable delocalisation within the ring. The only other example of a structurally characterised *N*-tosylated pyrazole is *N*-tosyl-4-(diacetoxyiodo)pyrazole, in which the sulfur out-of-plane deviations are 0.25, 0.23(1) Å [5]. Of interest here is the close approach of the solvate CH_2Cl_2 molecule [H(0a)···N(4) 2.61(3), H(0b)···O(31) 2.76(4) Å].

The desilylation of trimethylsilyl-substituted alkynes in the presence of KF followed by coordination to electron-rich metal fragments, such as $\text{Ru}(\text{PPh}_3)_2\text{Cp}$, has been described before [6]. This reaction is supposed to proceed via an intermediate vinylidene–ruthenium complex, which is subsequently deprotonated to give the isolated alkynyl–ruthenium derivative. However, if this course of reaction was followed here, the ruthenium



Scheme 1.

centre would be expected to be on the carbons originally bearing the SiMe₃ groups. In the present case, therefore, we propose that after proto-desilylation, the resulting alkyne is (unusually) π -coordinated to the ruthenium. Subsequent ready attack of the nucleophilic NHTs group on the terminal carbon of the coordinated alkyne, rendered electrophilic by coordination, results in cyclisation to the observed pyrazole, the ruthenium centre becoming σ -bonded to the central carbon. Such a reaction, which is sterically favoured by formation of the five-membered ring and by the proximity of the N-Ts group, might be useful synthetically, although we have not yet been able to find conditions under which **1** is the sole product. Other products formed during this reac-

tion appear to be relatively unstable and we have not yet been able to characterise them.

3. Experimental

3.1. General methods

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Solvents were dried, distilled and degassed before use, methanol was distilled over magnesium. Elemental analyses were from the Chemical and Micro-Analytical Services, Belmont, Victoria, Australia.

3.2. Instrumentation

Infra-red: Perkin-Elmer FT-IR 1920x. Nujol mull spectra were collected from samples mounted between NaCl discs (0.1 mm pathlength). NMR: Samples were dissolved in *d*⁶-acetone (Aldrich) using 5 mm sample tubes. Spectra were recorded using a Varian Gemini 2000 spectrometer (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.105 MHz). Electrospray mass spectra were measured with a Finnigan LCQ instrument, solutions being directly infused. The cyclic voltammogram was recorded for a 1.0 mM solution in CH₂Cl₂, with 0.1 M [NBu₄][BF₄] as supporting electrolyte, using a Mac-lab 400 instrument. A three-electrode system was used, consisting of a platinum-dot working electrode and Pt counter electrodes, with a saturated calomel electrode (SCE) as a reference electrode. Potentials are given in V vs SCE, the ferrocene-ferricinium couple being used as internal calibrant for the measured potentials (*E*₀ = 0.46 V vs SCE) [7].

3.3. Reagents

The compounds RuCl(dppe)Cp* [8] and SiMe₃-C≡CC(SiMe₃)=NNHTs [9] were prepared by standard literature methods. All other reagents were used as purchased from Aldrich.

RuCl(dppe)Cp* (100 mg, 0.15 mmol), SiMe₃-C≡CC(SiMe₃)=NNHTs (55 mg, 0.15 mmol) and KF (35 mg, 0.60 mmol) were dried under vacuum. Methanol (20 ml) was added and the suspension was heated at reflux point for 3 h. The solution was evaporated to dryness under vacuum and the bright yellow complex was extracted with toluene and loaded onto a silica gel column (10 cm). Elution with 1/9 acetone/hexane gave unreacted RuCl(dppe)Cp*. Elution with 3/7 acetone/hexane gave a bright yellow band that was evaporated to dryness to give Ru(C=CHNTsN=CH)(dppe)Cp* (**1**) (36 mg, 28%), crystallised from CH₂Cl₂/hexane. *Anal.* Calcd. (C₄₆H₄₈N₂O₂P₂RuS). C: 64.55; H: 5.62; N: 3.27; *M*, 856.

Found C: 64.83, H: 5.48, N: 3.04%. IR (Nujol): $\nu(\text{C}=\text{C})$ 1714 cm^{-1} . ^1H NMR: δ 7.56, 7.41 ($2 \times \text{d}$, J 7 Hz, 4H, C_6H_4), 7.39–7.09 (m, 20H, Ph), 6.33 (s, 1H, CH), 6.30 (s br, 1H, CH), 2.37 (s, 3H, Me), 2.35, 2.04 ($2 \times \text{m}$, $2 \times 2\text{H}$, CH_2), 1.44 (s, 15H, Cp^*). ^{13}C NMR: δ 160.13 (s, CH), 144.99, 137.38, 130.25, 128.21 ($4 \times \text{s}$, C_6H_4), 140.83–128.21 (m, Ph), 28.50 (m, CH_2), 21.59 (s, Me), 10.87 (s, $\text{Cp}^*\text{-Me}$). ^{31}P NMR: δ_{P} 86.32 (s, dppe). ES-MS (m/z): 857, $[\text{M} + \text{H}]^+$; 701, $[\text{M} - \text{Ts}]^+$.

3.4. Structure determination

A full sphere of diffraction data to $2\theta = 75^\circ$ was measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. 92732 reflections were merged to 23511 unique ($R_{\text{int}} = 0.044$) after “empirical”/multiscan absorption correction (proprietary software), 16281 with $F > 4\sigma(F)$ being used in the full matrix least squares refinement. All data were measured using monochromatic Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{\text{iso}})_{\text{H}}$ being refined. Conventional residuals were $R = 0.039$, $R_w = 0.042$ on $|F|$ [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the xTAL 3.7 program system [10]. Pertinent results are given in Fig. 1 (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 \AA) and its caption.

(1) $\text{Ru}(\text{C}=\text{CHNTsN}=\text{CH})(\text{dppe})\text{Cp}^* \cdot \text{CH}_2\text{Cl}_2 \equiv \text{C}_{46}\text{H}_{48}\text{N}_2\text{-O}_2\text{P}_2\text{RuS} \cdot \text{CH}_2\text{Cl}_2$, $M = 940.92$. Monoclinic, space group $P2_1/n$, $a = 17.1689(8) \text{ \AA}$, $b = 10.5027(5) \text{ \AA}$, $c = 25.843(1) \text{ \AA}$, $\beta = 106.339(1)^\circ$, $V = 4472 \text{ \AA}^3$, $Z = 4$. $D_c = 1.396 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.628 \text{ mm}^{-1}$, $T'_{\text{min,max}} = 0.70, 0.86$. Crystal size $0.32 \times 0.20 \times 0.07 \text{ mm}$.

4. Supplementary material

Full details of the structure determination (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 208849. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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