Tris(pyrazolyl)methanesulfonate (Tpms) − A Versatile Alternative to Tris(pyrazolyl)borate in Rhodium(I) Chemistry

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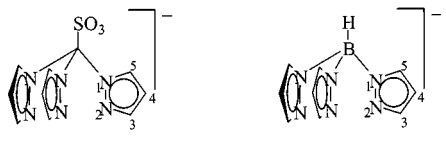
Thallium(I) tris(pyrazol-1-yl)methanesulfonate (TlTpms) has been prepared as a new versatile precursor for Tpms complexes. TlTpms readily reacts with the rhodium(I) complexes $[Rh(LL)Cl]_2$ [LL = $(CO)_2$, cod, nbd] to give the corresponding TpmsRh(LL) complexes [LL = $(CO)_2$ (**2a**), cod (**3**), and nbd (**4**)]. In solution, **2a** reversibly forms the binuclear complex TpmsRh(μ-CO)$_3$RhTpms (**2b**). **3** and **4** react with CO to form **2a**. TpmsRh(CO)(PR_3) complexes [PR_3 = PPh_3 (**5a**), PMe_3 (**5b**), PCy_3 (**5d**), $P(Ph)_2(PhSO_3K)$ (**5e**)] have been obtained by reaction of **2a** with the corresponding phosphanes. The solid-state structures of **2a**, **3**, **4**, and **5a** have been determined by X-ray analysis. **2a**, **3**, and **5a** have square-planar geometries with the Tpms ligand coordinating in a κ^2 mode. The non-coordinating pyrazole ring faces either away from (structure **2a**) or towards the rhodium atom (structures **3** and **5a**). **4** has a trigonal-bipyramidal coordination geometry with a genuine κ^3-bonded Tpms ligand. The non-rigid behaviour of the (Tpms)rhodium complexes has been followed by variable-temperature NMR studies. IR studies on **2a** and **5a–e** show that Tpms is a weakly donating ligand, comparable to the $Tp^{CF_3,Me}$ and Tp^{CF_3,CF_3} ligands. Compound **5e** is soluble and stable in dilute acids, showing that Tpms, unlike the Tp ligand, is hydrolytically stable.

Introduction

Since their original synthesis by Trofimenko in 1966,[1] tris(pyrazolyl)borates (Tp′)[2] have proved to be highly useful ligands and are widely used in the synthesis of novel transition metal complexes. Besides their advantages, which make them the most commonly used tripodal nitrogen ligands, tris(pyrazolyl)borates have the disadvantage of being unstable towards hydrolysis. This property can only be attenuated by using substituted pyrazoles in order to protect the labile B−N bonds.[3] Another problem is the low solubility of some (Tp)rhodium compounds. It has been reported several times that $TpRh(CO)_2$ could not be isolated. All attempts to synthesize this compound resulted in the formation of the highly insoluble TpRh(μ-CO)$_3$RhTp.[4]

We have recently reported[5] the synthesis of the novel tris(pyrazolyl)methanesulfonate ligand (Tpms), which was developed in analogy to the Tp ligand (Figure 1).



Trispyrazolylmethanesulfonate (Tpms) Trispyrazolylborate (Tp)

Figure 1. Analogy between Tpms and Tp

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Just like Tp, Tpms is a monoanionic, C_{3v}-symmetrical nitrogen-donor ligand. Instead of the boron hydride unit of Tp, Tpms has a methanesulfonate unit, which imparts very good stability towards hydrolysis and an increased solubility in polar solvents.

We describe herein the preparation of the thallium salt of Tpms as a precursor for ligand-exchange reactions and its reactions with $[Rh(LL)Cl]_2$ [LL = cod, nbd, $(CO)_2$]. The solid-state and solution structures of olefin, carbonyl, and phosphane derivatives of (Tpms)rhodium(I) are presented.

Results and Discussion

Synthesis of TlTpms (1)

TlTpms (**1**) was prepared by adding an excess of thallium(I) carbonate to an aqueous solution of LiTpms. After recrystallization from methanol, analytically pure **1** was obtained in 60% yield. The product **1** was found to react readily with transition metal halide complexes.

Although **1** only dissolves freely in water, it has proved to be surprisingly reactive under heterogeneous reaction conditions.

Synthesis of TpmsRh(CO)$_2$ (2a) and TpmsRh(μ-CO)$_3$RhTpms (2b)

Reaction of **1** with $[Rh(CO)_2Cl]_2$ in THF at room temperature gives the corresponding dicarbonyl complex $TpmsRh(CO)_2$ (**2a**) in excellent yield. Solutions of **2a** in THF are unstable and form a pale-yellow deposit. This deposit is highly insoluble in all common organic solvents and has been identified as TpmsRh(μ-CO)$_3$RhTpms (**2b**) by

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infrared spectroscopy. The characteristic asymmetric μ-CO stretching vibration is found at $\tilde{\nu} = 1860\ cm^{-1}$. The analogous binuclear Tp compound shows a CO stretching vibration at $\tilde{\nu} = 1845\ cm^{-1}$.[4c] This indicates that Tpms is a weaker donor than Tp. Unlike the Tp compound, the Tpms complex **2a** can be kept in solution under a carbon monoxide pressure of about 3 atm. Under these conditions, it is possible to grow yellow crystals of **2a** by diffusion-controlled crystallization from THF/pentane.

Compound **2a** is well soluble in polar organic solvents such as THF and acetone, but only sparingly soluble in less polar solvents such as toluene and dichloromethane. The rate of formation of **2b** appears to be strongly dependent on the concentration of **2a** in solution. At a concentration of 1 g/L under nitrogen, the first traces of **2b** become visible after 30 min. Under 3−4 atm of carbon monoxide pressure, no precipitate is formed within 4 weeks. When the concentration exceeds 2 g/L, the formation of **2b** can only be prevented by higher carbon monoxide pressures. Pressures of 40 atm of carbon monoxide and temperatures up to 80 °C are needed to recover **2a** from **2b** within 24 h.

Just like the tris(pyrazolyl)borates, Tpms is capable of acting as a bidentate or tridentate ligand and thus of forming 16- and 18-electron complexes with the Rh^I d^8-metal centre. NMR studies on **2a** show that all three pyrazoles are equivalent in solution at room temperature. This observation is consistent with either a non-rigid tridentate structure or a bidentate geometry with a dynamic exchange that is fast on the NMR time scale, as is often found in Tp chemistry.[6] In variable-temperature NMR spectra, the signal pattern of the pyrazoles changes from one consistent with C_{3v} symmetry at room temperature to one consistent with C_s symmetry at 203 K. With $\nu_{(CO)}$ stretching bands (sym and asym) of $\tilde{\nu} = 2091$, 2032, and 2023 cm^{-1} in KBr and of $\tilde{\nu} = 2098$, 2090, 2036, and 2024 cm^{-1} in THF, the vibrational frequencies are within the characteristic range for four-coordinate rhodium complexes.[6]

Moreover, the appearance of four bands indicates that there are two different isomers (A and B) in a κ^2-bonding mode (Figure 2).

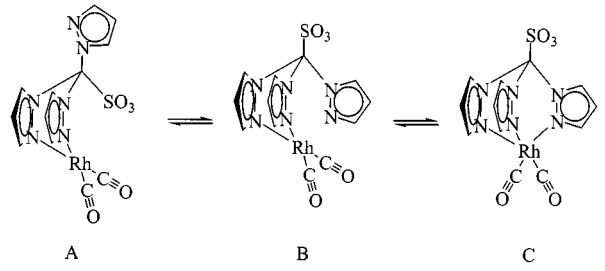

Figure 2. Three possible isomers of $TpmsRh(CO)_2$ (**2a**)

Although evidence for the existence of isomer C could not be observed by IR spectroscopic means, it is probably an intermediate in the dynamic equilibration of the pyrazoles observed by NMR, as ligand exchanges in square-planar d^8 complexes are known to proceed by an associative mechanism involving a five-coordinate intermediate.[7]

The electron-donating capabilities of a ligand can be estimated by comparing the CO stretching vibration bands of a *trans*-CO ligand. Table 1 shows a comparison between **2a** and $Tp'Rh(CO)_2$ compounds. The complexes $Tp^*Rh(CO)_2$,[6] $Tp^{Ph,Me}Rh(CO)_2$[8b] (**2d**), and $Tp^{CF_3,Me}Rh(CO)_2$[8c] (**2e**) show bands that are shifted towards lower energies compared to those of **2a**. Thus, the Tp′ ligands are evidently better donors. Only the highly fluorinated Tp^{CF_3,CF_3} ligand, which has been prepared in order to mimic fluorinated cyclopentadienyl ligands,[9] is a slightly weaker donor than the Tpms ligand. The donor properties of Tpms are intermediate between those of $Tp^{CF_3,Me}$ and Tp^{CF_3,CF_3} in analogous rhodium(I) compounds.

Table 1. CO stretching vibrations (KBr) of **2a** and analogous Tp′ complexes

Complex	ν_{sym}	ν_{asym}
$TpmsRh(CO)_2$ (**2a**)	2091	2023
		2032
$Tp^{Ph,Me}Rh(CO)_2$[8b] (**2d**)	2074	2003
$Tp^{CF_3,Me}Rh(CO)_2$[8c] (**2e**)	2082	2016
		2001
$Tp^{CF_3,CF_3}Rh(CO)_2$[8c]	2096	2038
$Tp^*Rh(CO)_2$[6]	2052	1972

X-ray Structure of 2a

Crystals of **2a** suitable for X-ray analysis were obtained by diffusion-controlled crystallization from THF/pentane. The mother liquor was kept under a carbon monoxide pressure throughout the crystallization in order to avoid the formation of **2b**. **2a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **2a** and one molecule of THF per cell unit. The ZORTEP plot given in Figure 3 shows one of the rhodium complexes of **2a**. Selected interatomic distances and angles are presented in Table 2.

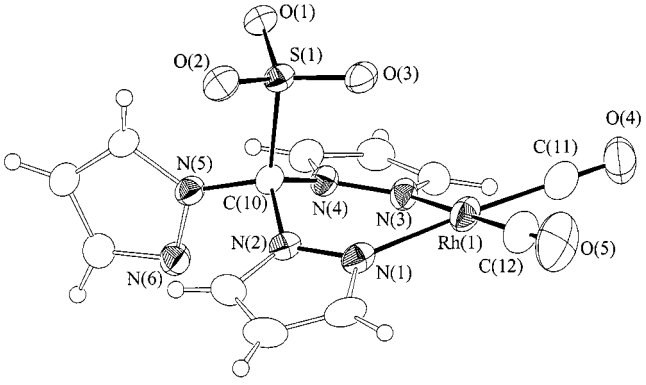

Figure 3. ZORTEP plot of $TpmsRh(CO)_2$ (**2a**) (50% probability)

The rhodium centre is coordinated in a slightly distorted planar geometry. The angle between the planes N(3)−Rh(1)−N(1) and C(11)−Rh(1)−C(12) is 3.0°, shifting the rhodium atom towards the oxygen atom O(3). Tpms acts as a bidentate ligand coordinating with two pyrazole

Table 2. Selected distances [Å] and angles [°] in $TpmsRh(CO)_2$ (**2a**)

Rh(1)−C(12)	1.851(3)	C(12)−Rh(1)−O(3)	105.43(11)
Rh(1)−C(11)	1.852(3)	C(11)−Rh(1)−O(3)	111.83(11)
Rh(1)−N(1)	2.060(2)	N(1)−Rh(1)−O(3)	71.19(7)
Rh(1)−N(3)	2.068(2)	N(3)−Rh(1)−O(3)	75.23(7)
Rh(1)−O(3)	2.8941(18)	O(3)−S(1)−C(10)	102.88(11)
S(1)−C(10)	1.882(3)	S(1)−O(3)−Rh(1)	120.91(10)
O(4)−C(11)	1.137(4)	N(2)−N(1)−Rh(1)	125.11(16)
O(5)−C(12)	1.132(4)	N(1)−N(2)−C(10)	122.5(2)
		N(4)−N(3)−Rh(1)	125.87(15)
C(12)−Rh(1)−C(11)	87.45(14)	N(3)−N(4)−C(10)	123.44(19)
C(12)−Rh(1)−N(1)	94.10(12)	N(6)−N(5)−C(10)	117.98(19)
C(11)−Rh(1)−N(1)	176.13(11)	N(2)−C(10)−N(4)	111.8(2)
C(12)−Rh(1)−N(3)	179.14(11)	N(5)−C(10)−S(1)	111.00(16)
C(11)−Rh(1)−N(3)	91.79(11)	N(2)−C(10)−S(1)	110.08(16)
N(1)−Rh(1)−N(3)	86.63(8)	N(4)−C(10)−S(1)	108.99(17)

Table 3. Selected distances [Å] and angles [°] in **2a**, **2c**, **2d**, and **2e**

Compound	Rh−N	Rh−C	C−O	N−Rh−N
$TpmsRh(CO)_2$ (**2a**)	2.060(2)	1.851(3)	1.137(4)	86.63(8)
	2.068(2)	1.852(3)	1.132(4)	
$[HTp^*Rh(CO)_2]BF_4$[8a] (**2c**)	2.070(4)	1.848(5)	1.127[34]	86.5(1)
	2.093(4)	1.867(6)	1.097[34]	
$Tp^{Ph,Me}Rh(CO)_2$[8b] (**2d**)	2.098(2)	1.851(3)	1.124(4)	86.79(10)
	2.102(2)	1.851(3)	1.134(4)	
$Tp^{CF_3,Me}Rh(CO)_2$[8c] (**2e**)	2.114(5)	1.824(7)	1.147[34]	82.7(2)
	2.116(4)	1.832(9)	1.145[34]	

moieties; one of the sulfonate oxygen atoms points towards the rhodium centre but the Rh(1)−O(3) distance of 2.8941(18) Å exceeds the sum of their van der Waals radii.

From the crystal structures of **2c**, **2d**, **2e**, and **2a** (Table 3), it is evident that the Tpms complex **2a** has the shortest Rh−N bond lengths, which can be attributed to the fact that this complex has the smallest steric demand. The bite angle of **2a** is similar to those found for **2c** and **2d**, but significantly larger than that reported for **2e**.

Synthesis of TpmsRh(cod) (3) and TpmsRh(nbd) (4)

Reactions of **1** with $[Rh(cod)Cl]_2$ and $[Rh(nbd)Cl]_2$ in dichloromethane at room temperature give the corresponding complexes TpmsRh(cod) (**3**) and TpmsRh(nbd) (**4**) in very high yields. Both products were found to be well soluble in most organic solvents. At room temperature, both compounds show ^1H NMR patterns in agreement with C_{3v} symmetry. Again, this is consistent with either a non-rigid κ^3-bonded structure or a κ^2-mode geometry with a dynamic exchange that is fast on the NMR time scale down to 203 K. The methylene protons of the cyclooctadiene allow an assignment of the pyrazole protons by means of NOESY experiments. Complex **3** exhibits peaks at δ = 8.50, 7.68, and 6.55 attributable to the protons attached to C^5, C^3, and C^4, respectively. The corresponding peaks for TpRh(cod) are found at δ = 7.76, 7.58, and 6.21 (not fully assigned).[6]

The prominent downfield shift of the signal of the proton attached to C^5 in Tpms is caused by the deshielding effect of the sulfonate group. The $-I$ effect of the sulfonate group renders the pyrazole groups in the Tpms ligand less electron-rich, whereas the $+I$ effect of the BH group has the opposite effect.

Complexes **3** and **4** readily react with carbon monoxide to give **2a** [Equation (1)]. In the reverse reaction, considerable amounts of **2b** are formed.

$$TpmsRh(LL) \xrightarrow[-\,[LL]]{3 - 4\ atm.\ CO} TpmsRh(CO)_2 \qquad (1)$$

[LL] = 1,5-cyclooctadiene, norbornadiene

X-ray Structure of 3

Crystals of **3** suitable for X-ray analysis were obtained by diffusion-controlled crystallization from dichloromethane/pentane. This complex crystallizes as rods in the monoclinic space group $P2(1)/c$. Figure 4 shows a ZORTEP view of **3**. Selected interatomic distances and angles are given in Table 4.

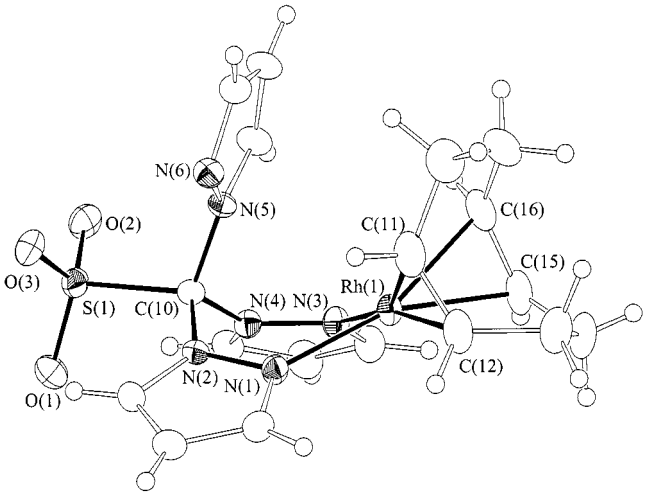

Figure 4. ZORTEP plot of TpmsRh(cod) (**3**) (50% probability)

The rhodium centre adopts a slightly distorted planar geometry with Tpms coordinating as a bidentate ligand. The third pyrazole ring is orientated parallel to the C(11)−Rh(1)−C(16) plane. The distance between the non-coordinating nitrogen atom N(6) and the rhodium centre Rh(1) is 3.535 Å, which exceeds the sum of their van der Waals radii. N(1), N(3), M(1), and M(2) [M(1) and M(2) are the centres of the bond between the olefinic carbon atoms C(11)−C(12) and C(15)−C(16)] deviate from a plane calculated by least-squares fitting by less than 0.05 Å. The rhodium centre is not significantly displaced from this plane. Comparison with the structurally characterized complexes $Tp^{4Bo,3Me}Rh(cod)$,[10] $Tp^{iPr,iPr}Rh(cod)$,[11] $Tp^{Ph}Rh(cod)$,[12] and $B(pz)_4Rh(cod)$[13] shows that the Rh−N and Rh−C bond lengths are equal within experimental errors. Only the bite angles show significant variations. The N−Rh−N angle in **3** [85.46(7)°] resembles the angles in $B(pz)_4Rh(cod)$ [86.6(1)°] and $Tp^{Ph}Rh(cod)$ [84.56(24)°]. The corresponding angles in $Tp^{iPr,iPr}Rh(cod)$

Table 4. Selected distances [Å] and angles [°] in TpmsRh(cod) (**3**)

Rh(1)−N(1)	2.0895(18)	C(16)−Rh(1)−C(12)	90.01(10)
Rh(1)−N(3)	2.1025(18)	C(15)−Rh(1)−C(12)	81.17(10)
Rh(1)−C(11)	2.121(2)	N(2)−N(1)−Rh(1)	122.39(13)
Rh(1)−C(16)	2.125(2)	N(1)−N(2)−C(10)	119.44(16)
Rh(1)−C(15)	2.138(2)	N(4)−N(3)−Rh(1)	121.13(13)
Rh(1)−C(12)	2.140(2)	N(3)−N(4)−C(10)	118.90(16)
S(1)−C(10)	1.891(2)	N(6)−N(5)−C(10)	120.94(17)
N(2)−C(10)	1.450(3)	C(9)−N(5)−C(10)	126.22(18)
N(4)−C(10)	1.465(3)	N(2)−C(10)−N(5)	109.75(16)
N(5)−C(10)	1.454(3)	N(2)−C(10)−N(4)	109.94(16)
C(11)−C(12)	1.386(4)	N(5)−C(10)−N(4)	107.42(16)
C(15)−C(16)	1.386(4)	N(2)−C(10)−S(1)	110.83(14)
		N(5)−C(10)−S(1)	108.75(14)
N(1)−Rh(1)−N(3)	85.46(7)	N(4)−C(10)−S(1)	110.08(13)
N(1)−Rh(1)−C(11)	90.18(9)	C(12)−C(11)−C(18)	125.6(2)
N(3)−Rh(1)−C(11)	157.45(9)	C(12)−C(11)−Rh(1)	71.74(14)
N(1)−Rh(1)−C(16)	160.40(9)	C(18)−C(11)−Rh(1)	110.98(19)
N(3)−Rh(1)−C(16)	95.07(9)	C(11)−C(12)−C(13)	122.5(2)
C(11)−Rh(1)−C(16)	81.82(11)	C(11)−C(12)−Rh(1)	70.30(14)
N(1)−Rh(1)−C(15)	161.64(9)	C(13)−C(12)−Rh(1)	113.73(17)
N(3)−Rh(1)−C(15)	93.86(8)	C(16)−C(15)−C(14)	125.8(2)
C(11)−Rh(1)−C(15)	97.06(10)	C(16)−C(15)−Rh(1)	70.51(14)
C(16)−Rh(1)−C(15)	37.95(11)	C(14)−C(15)−Rh(1)	110.13(18)
N(1)−Rh(1)−C(12)	94.64(8)	C(15)−C(16)−C(17)	124.2(2)
N(3)−Rh(1)−C(12)	164.47(9)	C(15)−C(16)−Rh(1)	71.54(14)
C(11)−Rh(1)−C(12)	37.95(11)	C(17)−C(16)−Rh(1)	112.98(19)

[82.5(1)°] and $Tp^{4Bo,3Me}$Rh(cod) [82.3(2)°] are smaller, probably as a consequence of the levering effect of the bulky substituents in the 5-position of the pyrazoles.[3a]

X-ray Structure of 4

The norbornadiene complex **4** crystallizes in the form of dark-yellow plates in the orthorhombic space group *Pnma*. The ZORTEP plot is shown in Figure 5 and selected interatomic distances and angles are presented in Table 5. Unlike the other structurally characterized Tpms rhodium complexes, **4** has a distorted trigonal-bipyramidal coordination geometry with a genuine κ^3-bonded Tpms ligand. The pyrazole groups of the tripod occupy one axial and two equatorial coordination sites. The atoms N(1), N(1a), Rh(1), C(8), and C(8a) lie in the equatorial plane, while the "axis" N(3)−Rh(1)−M(3) [M(3) is the centre of the bond between the olefinic carbon atoms C(10)−C(10a)] is bent by 10.5°.

The structure resembles those of Tp^{Me}Rh(nbd)[6] (**4a**) and $Tp^{iPr,iPr}$Rh(nbd)[11] (**4b**), where the Tp′ ligands are also bonded in a κ^3-fashion, while in Tp^{Ph}Rh(nbd)[12] and $B(pz)_4$Rh(nbd),[13] the polypyrazolylborates coordinate in a κ^2-mode forming planar complexes. The X-ray analysis shows that all Rh−N separations are significantly shorter in **4** than those in **4a** and **4b** (Table 6), while the Rh−C separations as well as the C=C distances are the same within experimental errors. It is noteworthy that the Rh−N distances to the axially coordinated pyrazole ring in **4**, **4a**, and **4b** are significantly shorter than those to the equatorially coordinated rings. The reason for this is not clear. As a rule, axial bonds are longer than equatorial bonds in trigonal-bipyramidal compounds. However, relatively few trigonal-bipyramidal rhodium(I) complexes are known.[14] A structure correlation analysis of d^8 five-coordinated complexes does not shed any light on the role of trigonal-bipyramidal geometry in favouring the S_N2 pathway in rhodium(I) complexes.[15]

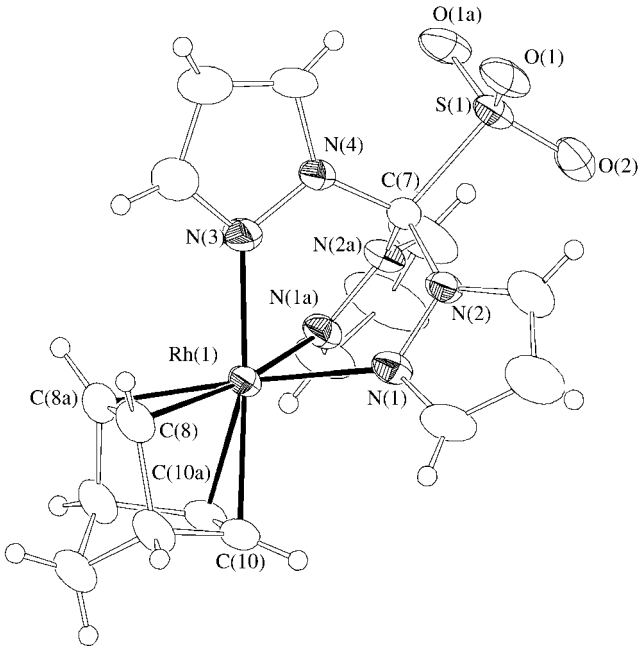

Figure 5. ZORTEP plot of TpmsRh(nbd) (**4**) (50% probability)

Table 5. Selected distances [Å] and angles [°] in TpmsRh(nbd) (**4**)

Rh(1)−N(3)	2.064(3)	C(8)a−Rh(1)−N(1)a	120.79(11)
Rh(1)−C(8)	2.065(3)	C(10)−Rh(1)−N(1)a	117.13(10)
Rh(1)−C(8)a	2.065(3)	C(10)a−Rh(1)−N(1)a	93.09(10)
Rh(1)−C(10)	2.151(3)	N(3)−Rh(1)−N(1)	82.45(9)
Rh(1)−C(10)a	2.151(3)	C(8)−Rh(1)−N(1)	120.79(11)
Rh(1)−N(1)a	2.218(2)	C(8)a−Rh(1)−N(1)	161.15(11)
Rh(1)−N(1)	2.218(2)	C(10)−Rh(1)−N(1)	93.09(10)
S(1)−C(7)	1.895(4)	C(10)a−Rh(1)−N(1)	117.13(10)
N(2)−C(7)	1.464(3)	N(1)a−Rh(1)−N(1)	77.98(11)
N(4)−C(7)	1.455(5)	N(2)−N(1)−Rh(1)	119.95(16)
C(7)−N(2)a	1.464(3)	N(1)−N(2)−C(7)	119.1(2)
C(8)−C(8)a	1.426(7)	N(4)−N(3)−Rh(1)	123.2(2)
C(10)−C(10)a	1.375(6)	N(3)−N(4)−C(7)	119.7(3)
		N(4)−C(7)−N(2)	110.08(19)
N(3)−Rh(1)−C(8)	97.57(12)	N(4)−C(7)−N(2)a	110.08(19)
N(3)−Rh(1)−C(8)a	97.57(12)	N(2)−C(7)−N(2)a	109.6(3)
C(8)−Rh(1)−C(8)a	40.40(19)	N(4)−C(7)−S(1)	109.2(2)
N(3)−Rh(1)−C(10)	158.69(9)	N(2)−C(7)−S(1)	108.94(17)
C(8)−Rh(1)−C(10)	66.80(12)	N(2)a−C(7)−S(1)	108.94(17)
C(8)a−Rh(1)−C(10)	80.02(12)	C(8)a−C(8)−C(9)	105.64(18)
N(3)−Rh(1)−C(10)a	158.69(9)	C(8)a−C(8)−Rh(1)	69.80(9)
C(8)−Rh(1)−C(10)a	80.02(12)	C(9)−C(8)−Rh(1)	99.27(19)
C(8)a−Rh(1)−C(10)a	66.80(12)	C(10)a−C(10)−C(9)	106.67(18)
C(10)−Rh(1)−C(10)a	37.26(17)	C(10)a−C(10)−Rh(1)	71.37(8)
N(3)−Rh(1)−N(1)a	82.45(9)	C(9)−C(10)−Rh(1)	95.80(18)
C(8)−Rh(1)−N(1)a	161.15(11)		

Synthesis of TpmsRh(CO)PPh_3 (5a), TpmsRh(CO)PMe_3 (5b), and TpmsRh(CO)PCy_3 (5c)

All phosphane complexes were synthesized by adding the phosphane to a THF solution of **2a**. The highly basic tri-

Table 6. Selected distances [Å] and angles [°] in **4**, **4a**, and **4b**

Compound	Rh−N	Rh−C	C=C	N−Rh−N
TpmsRh(nbd) (**4**)	2.064(3)	2.065(3)	1.375(6)	77.98(11)
	2.218(2)	2.065(3)	1.426(7)	82.45(9)
	2.218(2)	2.151(3)		82.45(9)
		2.151(3)		
$Tp^{Me}Rh(nbd)$[6] (**4a**)	2.147(7)	2.07(1)	1.37(3)	89.6(4)
	2.247(9)	2.09(1)	1.45(3)	82.2(3)
	2.25(1)	2.154(8)		82.4(4)
		2.16(1)		
$Tp^{iPr,iPr}Rh(nbd)$[11] (**4b**)	2.146(4)	2.069(5)	1.364(6)	90.4(1)
	2.260(4)	2.074(5)	1.448(6)	82.5(1)
	2.273(4)	2.137(5)		81.5(1)
		2.149(4)		

Table 7. $^{31}P\{^1H\}$ NMR and IR data of **5a**−**5c** and selected Tp′ compounds

Compound	$\delta^{31}P$ [ppm]	$^1J_{RhP}$ [Hz]	ν_{CO}[a] [cm^{-1}]
TpmsRh(CO)PPh_3 (**5a**)	44	158	2000
Tp*Rh(CO)PPh_3[17] (**5e**)	42.55	162	1978[b]
$Tp^{Ph,Me}$Rh(CO)PPh_3[8b] (**5f**)	42.39	164	1983
TpRh(CO)PPh_3[19] (**5h**)	44	156	1978
TpmsRh(CO)PMe_3 (**5b**)	2.6	148	1990
Tp*Rh(CO)PMe_3[18] (**5g**)	6.05	146	1961[b]
TpmsRh(CO)PCy_3 (**5c**)	52	153	1978
TpRh(CO)PCy_3[19] (**5i**)			1947

[a] KBr. − [b] CH_2Cl_2.

methylphosphane had to be added slowly in stoichiometric amounts in order to avoid displacement of the second carbon monoxide ligand or the tripod, as was observed in the case of Tp*Rh$(C_2H_4)_2$.[16] The less basic and sterically more crowded tricyclohexyl- and triphenylphosphane could be added in excess. The displacement of carbon monoxide is a fast reaction; it was not necessary to work under carbon monoxide pressure in order to avoid the formation of **2b**. The corresponding TpmsRh(CO)PR_3 complexes were obtained as bright-yellow crystals in excellent yields. They were found to be well soluble in most organic solvents.

At room temperature, all TpmsRh(CO)PR_3 compounds show ^1H NMR patterns in agreement with C_{3v} symmetry, indicating rapid exchange of the pyrazoles on the NMR time scale. ^1H NMR studies on **5a** show that two pyrazole groups become equivalent at 203 K, displaying a 2:1 intensity ratio, which is consistent with a C_s-symmetric complex or a fast exchange of only two pyrazole groups. Similar effects have been observed for the corresponding Tp′ compounds Tp*Rh(CO)PPh_3[17] (**5e**), $Tp^{Ph,Me}$Rh(CO)PPh_3[8b] (**5f**), and Tp*Rh(CO)PMe_3[18] (**5g**). The exchange mechanisms for **5f** and **5g** were suggested to proceed via trigonal-bipyramidal intermediates. The $\Delta G^{\neq}$ values estimated from the coalescence temperatures were 76.5 kJ/mol for the bulky **5f**[8b] and 63 kJ/mol for the less bulky **5g**.[18] As **5a** is even less sterically hindered, it is consistent that its $\Delta G^{\neq}$ value is considerably smaller (46±2 kJ/mol). It can be assumed that the exchange takes place between the free nitrogen atom N(6) and the nitrogen atom N(3) lying *trans* to the CO ligand, because the $\Delta G^{\neq}$ value is similar to those estimated for **2a** (47±2 kJ/mol) and **5b** (47±2 kJ/mol). This is consistent with the fact that CO has a larger *trans* effect than PR_3.[7] The $^{31}P\{^1H\}$ NMR spectrum of **5a** shows a doublet at $\delta = 44$ ($^1J_{RhP} = 158$ Hz), which is comparable with those of **5e**, **5f**, and TpRh(CO)PPh_3[19] (**5h**) (Table 7).

The CO stretching vibration of **5a** is found at considerably higher energy than those of **5e**, **5f**, and **5h**. This indicates that the electronic properties of the tripod have a big influence on the CO stretching vibration. Comparison of the Tp′ compounds **5e**, **5f**, and **5h** shows that the steric properties of the ligands have only small effects on the CO stretching vibration. A similar conclusion is reached on comparing **5b** and **5c** with the corresponding Tp′ compounds **5g** and **5i**.

X-ray Structure of 5a

The Tpms complex **5a** crystallizes as thin rods in the triclinic space group $P\bar{1}$. The asymmetric unit contains one molecule of **5a** and one molecule of THF. Figure 6 shows a ZORTEP plot of **5a**, and a selection of interatomic distances and angles is given in Table 8.

The rhodium atom is coordinated in a slightly distorted planar geometry. The Tpms coordinates as a bidentate ligand and the non-coordinating pyrazole group is located above the coordination plane. The distance between Rh(1) and the non-coordinating N(6) is 3.513 Å, which exceeds the sum of their van der Waals radii. The different *trans* effects of PPh_3 and CO are not manifested in different bond lengths Rh(1)−N(3) [2.100(3) Å] and Rh(1)−N(1) [2.093(3) Å].

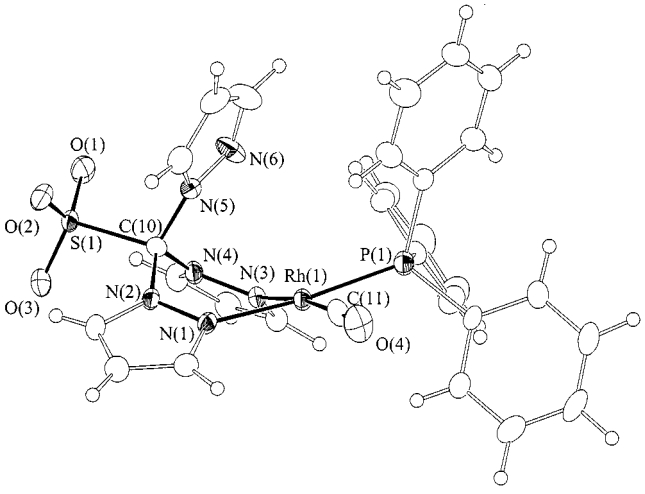

Figure 6. ZORTEP plot of TpmsRh(CO)PPh_3 (**5a**) (50% probability)

Table 8. Selected distances [Å] and angles [°] in $TpmsRh(CO)PPh_3$ (**5a**)

Rh(1)−C(11)	1.816(4)	C(12)−P(1)−C(18)	106.06(17)
Rh(1)−N(1)	2.093(3)	C(12)−P(1)−C(24)	103.28(17)
Rh(1)−N(3)	2.100(3)	C(18)−P(1)−C(24)	102.97(19)
Rh(1)−P(1)	2.2734(13)	C(12)−P(1)−Rh(1)	111.49(14)
P(1)−C(12)	1.825(4)	C(18)−P(1)−Rh(1)	115.07(12)
P(1)−C(18)	1.827(4)	C(24)−P(1)−Rh(1)	116.71(12)
P(1)−C(24)	1.828(4)	N(2)−N(1)−Rh(1)	122.9(2)
S(1)−C(10)	1.893(4)	N(1)−N(2)−C(10)	119.2(3)
O(4)−C(11)	1.148(5)	N(4)−N(3)−Rh(1)	122.7(3)
N(2)−C(10)	1.472(4)	N(3)−N(4)−C(10)	120.2(3)
N(4)−C(10)	1.440(5)	N(6)−N(5)−C(10)	119.8(3)
N(5)−C(10)	1.453(5)	C(9)−N(5)−C(10)	126.9(3)
		N(4)−C(10)−N(5)	109.3(3)
C(11)−Rh(1)−N(1)	92.24(14)	N(4)−C(10)−N(2)	110.5(3)
C(11)−Rh(1)−N(3)	172.68(14)	N(5)−C(10)−N(2)	108.2(3)
N(1)−Rh(1)−N(3)	84.09(12)	N(4)−C(10)−S(1)	111.0(2)
C(11)−Rh(1)−P(1)	87.20(12)	N(5)−C(10)−S(1)	109.1(2)
N(1)−Rh(1)−P(1)	174.21(9)	N(2)−C(10)−S(1)	108.7(2)
N(3)−Rh(1)−P(1)	97.09(9)	O(4)−C(11)−Rh(1)	176.3(3)

Synthesis of $TpmsRh(CO)PPh_2PhSO_3K·H_2O$ (5d)

An excess of $PPh_2PhSO_3K·H_2O$ was added to a THF solution of the dicarbonyl compound **2a**. As this is a slow heterogeneous reaction, it was necessary to keep the mixture under carbon monoxide pressures of about 3 atm in order to avoid formation of the binuclear compound **2b**. The resulting complex **5d** was found to be soluble in wet THF and could be separated from the excess phosphane by filtration. It was then precipitated by overlaying the THF solution with pentane.

Compound **5d** was found to be well soluble in water, but formed colloidal rhodium within a few minutes. This decomposition of the complex was evidently not triggered by decomposition of the ligands, as free Tpms as well as the phosphane could be detected. We suspect that the rhodium centre is attacked by hydroxy ions, which leads to redox reactions and thus to decomposition of the complex. Indeed, it was found that the decomposition could be prevented by dissolving **5d** in very dilute phosphoric or sulfuric acid (pH = 3−4). Tpms is stable under these conditions.[5] At lower pH values, Tpms is protonated and thus loses its coordinative ability towards the rhodium centre. All three pyrazole groups are seen to be equivalent according to the ^1H NMR spectrum. The signals are slightly broadened at room temperature. We could not obtain single crystals of **5d**, but the similarity of its NMR and IR data to those of **5a** is evident.

Conclusion

The thallium salt of the novel ligand Tpms is a convenient starting material for the preparation of rhodium(I) complexes. The sulfonate group of Tpms ensures good solubility in polar solvents. This has allowed the isolation of the planar dicarbonyl complex $TpmsRh(CO)_2$ (**2a**). The corresponding complex of the Trofimenko ligand Tp is not sufficiently stable for a crystal structure analysis. The IR data (ν_{CO}) indicate that Tpms is a remarkably weaker donor than the Tp ligand in carbonylrhodium(I) complexes. Its donor strength is similar to that of the Tp^{CF_3,CF_3} ligand. The lower donor strength of Tpms does not result in longer rhodium−nitrogen bonds. In fact, the X-ray structures of $TpmsRh(CO)_2$ (**2a**) and TpmsRh(nbd) (**4**) show that Tpms forms shorter rhodium−nitrogen bonds than the sterically more demanding Tp ligands (Tp^{Me}, $Tp^{CF_3,Me}$, $Tp^{Ph,Me}$, $Tp^{iPr,iPr}$) in analogous compounds.

It is noteworthy that the Tpms ligand acts as a bis(chelating) ligand in TpmsRh(cod) (**3**) but as a tris(chelating) ligand in TpmsRh(nbd) (**4**). We can see no obvious reason for this behaviour. $TpRh^I$ complexes with a coordination number of five are very rare. To the best of our knowledge, $Tp^{iPr,iPr}$ is the only other Tp ligand that has been shown to act both as a bidentate and as a tridentate ligand in rhodium(I) complexes.[11] Jones et al. have found that the hapticity of Tp ligands correlates with the ^{11}B chemical shift.[20] The corresponding probe for the Tpms ligand would be the ^{13}C chemical shift of the methanesulfonato carbon atom. However, the ^{13}C chemical shifts for the structurally characterized compounds **3**, **4**, and **5a** are not significantly different. Thus, these data do not correlate with the solid-state structures, leaving the denticity of the Tpms ligand in solution ambiguous.

According to our preliminary experiments, all the $TpmsRh^I$ compounds described herein can be used as precursors for catalysts in hydroformylation reactions. We are currently investigating the differences between the ligands Tpms and Tp in rhodium-catalyzed reactions.

Experimental Section

General Remarks: The compounds tris(pyrazolyl)methane,[21] LiTpms,[5] $[\{Rh(CO)_2Cl\}_2]$,[22] $[\{Rh(nbd)Cl\}_2]$,[23] $[\{Rh(cod)Cl\}_2]$,[24] and $P(C_6H_5)_2(p\text{-}C_6H_4\text{-}SO_3K)·H_2O$[25] were synthesized according to literature procedures. All other reagents were commercial samples and were used as received. All reactions were carried out under nitrogen using standard Schlenk techniques unless stated otherwise. Solvents were purified and degassed by standard procedures. Methanol and ethanol used in the work-up of **1** were used without further purification. Filtration was carried out using 1-μm membrane filters (regenerated cellulose, Schleicher & Schuell). Reactions under 3−4 atm pressure were performed in glass tubes equipped with Teflon seals and valves. ***All operations in glass vessels at elevated pressures should be performed using effective body and face protection!*** − One-dimensional ^1H, ^{31}P, and ^{13}C NMR spectra were recorded with Bruker DRX 200 (at 293 K) or Bruker DRX 500 (at 298 K) spectrometers. Two-dimensional NOESY and COSY as well as one-dimensional DEPT spectra were recorded with a Bruker DRX 500 spectrometer. Chemical shifts (δ) are given in ppm referenced to the solvent peak. Spectra recorded using $[D_8]$THF as a solvent were referenced to tetramethylsilane. Spectra recorded using D_2O as a solvent were referenced to sodium

3-(trimethylsilyl)-1-propanesulfonate. The spectrum of **5d** was recorded in dilute D_3PO_4 solution (pH = 3−4), which was prepared from D_2O and P_4O_{10} under inert conditions. Chemical shifts were ±0.01 ppm for δ^1H, ±0.1 ppm for $\delta^{31}P$ and ±0.1 ppm for $\delta^{13}C$. − Infrared spectra were recorded with a Bruker IFS 66 FT spectrometer. − Electron impact (EI) mass spectra were recorded with a Varian MAT 311 A instrument with an ionization energy of 70 eV. FAB mass spectra were recorded with a Finnigan MAT 8200 instrument using an NBA matrix. − Elemental analyses were performed using a Perkin−Elmer CHN-2400/II elemental analyzer.

Thallium(I) Tris(pyrazol-1-yl)methanesulfonate, TlTpms (1): A solution of tris(pyrazolyl)methane (4.9 g, 23 mmol) in THF (100 mL) was cooled to −78 °C and a 1.6 M solution of *n*-butyllithium (16 mL, 26 mmol) was slowly added. The solution was stirred for 1 h while the temperature was allowed to rise to 0 °C. After subsequent cooling to −60 °C, trimethylamine−sulfur trioxide (4.2 g, 30 mmol) was added and the resulting suspension was stirred overnight while the temperature was allowed to rise to 25 °C. The mixture was then filtered through a membrane filter and the solid residue was added to a solution of thallium(I) carbonate (7.1 g, 15 mmol) in water (150 mL). The resulting mixture was stirred at 60−70 °C for 1 h and then the solvent was evaporated under reduced pressure. The residue was extracted for 4 h with wet ethanol to remove less polar by-products. The remaining residue was recrystallized from 1 L of wet methanol to give 6.9 g of colourless crystals (60%). − ^1H NMR (200 MHz, D_2O): δ = 6.56 (dd, $^3J_{HH}$ = 2.7 Hz, $^3J_{HH}$ = 1.8 Hz, 3 H, pyrazolyl 4-H), 7.65 (dd, $^3J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 0.6 Hz, 3 H, pyrazolyl 3-/5-H), 7.75 (dd, $^3J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 0.6 Hz, 3 H, pyrazolyl 3-/5-H). − $^{13}C\{^1H\}$ NMR (500 MHz, D_2O): δ = 98.7 (s, C−SO_3), 110.5 (s, pyrazolyl C^4), 135.2 (s, pyrazolyl $C^{3/5}$), 145.4 (s, pyrazolyl $C^{3/5}$). − IR (KBr): $\tilde{\nu}$ = 3150 cm^{-1}, 3137 (w, C−H), 1522 (s, C=C), 1089, 1059, 1052, 1039 (s, S=O). − MS (FAB^+): *m/z* (%) = 499 (1.3) $[M + H]^+$. − $C_{10}H_9N_6O_3STl$ (497.7): calcd. C 24.00, H 1.81, N 16.79; found C 24.04, H 1.80, N 16.87.

Dicarbonyl[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), $TpmsRh(CO)_2$ (2a): A mixture of the carbonylrhodium chloride complex $[\{Rh(CO)_2Cl\}_2]$ (78 mg, 0.20 mmol) and **1** (0.20 g, 0.40 mmol) in THF (200 mL) was pressurized with 3−4 atm of carbon monoxide and stirred for 16 h at room temperature. Thereafter, the precipitated TlCl was allowed to settle and the supernatant solution was siphoned into another vessel by means of a cannula. From the clear yellow solution, 0.19 g (100%) of **2a** was obtained. To obtain yellow crystals of **2a** suitable for X-ray analysis, the solution was overlaid with pentane, pressurized with 3−4 atm of carbon monoxide, and left until crystallization occurred. − ^1H NMR (200 MHz, [D_6]acetone): δ = 6.73 (dd, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 2.1 Hz, 3 H, pyrazolyl 4-H), 8.19 (d, $^3J_{HH}$ = 2.1 Hz, 3 H, pyrazolyl 3-/5-H), 8.24 (d, $^3J_{HH}$ = 3.0 Hz, 3 H, pyrazolyl 3-/5-H).[26] − IR (KBr): $\tilde{\nu}$ = 3169 cm^{-1}, 3152 (w, C−H), 1520 (s, C=C), 2091, 2032, 2023 (vs, C=O) 1086, 1073, 1054, 1040 (s, S=O). − MS (FAB^+): *m/z* (%) = 453 (5.6) $[M + H]^+$. − $C_{12}H_9N_6O_5RhS$ (452.2): calcd. C 31.87, H 2.01, N 18.58; found C 32.13, H 2.20, N 18.49.

μ-Tricarbonylbis{[tris(pyrazol-1-yl)methanesulfonato]rhodium(I)}, $TpmsRh(\mu\text{-}CO)_3RhTpms$ (2b): Compound **2b** was formed when a solution of **2a** in THF was left without a positive pressure of carbon monoxide. The solvent was slowly evaporated from a solution of **2a** (45 mg, 0.10 mmol) in THF by passing a gentle stream of nitrogen over it. After 2 d, the residue was dried in vacuo to give 44 mg (100%) of **2b** as an amorphous pale-yellow powder. − IR (KBr): $\tilde{\nu}$ = 3191 cm^{-1}, 3150, 3110 (m, C−H), 1861 (vs, C=O), 1522 (s, C=C), 1081, 1068, 1051 (s, S=O). − $C_{23}H_{18}N_{12}O_9Rh_2S_2$ (876.4): calcd. C 31.52, H 2.07, N 19.18; found C 31.82, H 2.42, N 18.82.

(Cycloocta-1,5-diene)[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), TpmsRh(cod) (3): A mixture of the (cyclooctadiene)rhodium chloride complex $[\{Rh(cod)Cl\}_2]$ (99 mg, 0.20 mmol) and **1** (0.20 g, 0.40 mmol) in dichloromethane (50 mL) was stirred for 16 h at room temperature. The precipitated TlCl was then separated by filtration. Evaporation of the solvent from the filtrate afforded 0.20 g (100%) of **3** as a yellow powder. To obtain yellow crystals of **3** suitable for X-ray analysis, the filtrate was concentrated to 10% of its original volume and then overlaid with pentane. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.9 (m, 4 H, cod CH_2), 2.3 (m, 4 H, cod CH_2), 4.15 (br. s, 4 H, cod CH), 6.55 (dd, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 2.1 Hz, 3 H, pyrazolyl 4-H), 7.68 (d, $^3J_{HH}$ = 2.1 Hz, 3 H, pyrazolyl 3-H), 8.50 (br. s, 3 H, pyrazolyl 5-H). − $^{13}C\{^1H\}$ NMR (500 MHz, CD_2Cl_2): δ = 29.2 (s, cod CH_2), 82.6 (d, $^1J_{RhC}$ = 12.7 Hz, cod = CH), 93.4 (s, C−SO_3), 106.5 (s, pyrazolyl C^4), 135.1 (s, pyrazolyl C^5), 141.2 (s, pyrazolyl C^3). − IR (KBr): $\tilde{\nu}$ = 3165 cm^{-1}, 3148, 3111 (m, C−H), 1521 (s, C=C), 1086, 1081, 1054, 1043 (s, S=O). − MS (EI, 300 °C): *m/z* (%) = 504 (12.7) $[M]^+$, 424 (1.9) $[M - SO_3]^+$, 357 (62.2) $[M - SO_3 - C_3H_3N_2]^+$. − $C_{18}H_{21}N_6O_3RhS$ (504.4): calcd. C 42.86, H 4.20, N 16.66; found C 42.67, H 4.26, N 16.74.

(Bicyclo[2.2.1]hepta-2,5-diene)[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), TpmsRh(nbd) (4): A mixture of the (norbornadiene)rhodium chloride complex $[\{Rh(nbd)Cl\}_2]$ (23 mg, 0.050 mmol) and **1** (50 mg, 0.10 mmol) in dichloromethane (30 mL) was stirred for 16 h at room temperature. The precipitated TlCl was then separated by membrane filtration. Evaporation of the solvent from the filtrate afforded 48 mg (100%) of **4** as a yellow powder. To obtain dark-yellow crystals of **4** suitable for X-ray analysis, the filtrate was concentrated to 10% of its original volume and then overlaid with pentane. − ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.38 (br. s, 2 H, nbd CH_2), 3.89 (br. s, 4 H, nbd =CH), 3.90 (br. s, 2 H, nbd CH), 6.50 (dd, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 2.0 Hz, 3 H, pyrazolyl 4-H), 7.55 (d, $^3J_{HH}$ = 2.0 Hz, 3 H, pyrazolyl 3-H), 8.20 (d, 3 H, $^3J_{HH}$ = 2.8 Hz, pyrazolyl 5-H). − $^{13}C\{^1H\}$ NMR (500 MHz, CD_2Cl_2): δ = 49.4 (d, $^2J_{RhC}$ = 2.6 Hz, nbd CH), 52.6 (d, $^1J_{RhC}$ = 11.2 Hz, nbd =CH), 60.4 (d, $^3J_{RhC}$ = 6.9 Hz, nbd CH_2), 93.5 (s, C−SO_3), 106.1 (s, pyrazolyl C^4), 134.6 (s, pyrazolyl C^5), 141.2 (s, pyrazolyl C^3). − IR (KBr): $\tilde{\nu}$ = 3142 cm^{-1}, 3121, 2994, 2898 (m, C−H), 1523 (s, C=C), 1083, 1068, 1053 (s, S=O). − MS (EI, 320 °C): *m/z* (%) = 488 (16.5) $[M]^+$, 408 (7.4) $[M - SO_3]^+$, 341 (100.0) $[M - SO_3 - C_3H_3N_2]^+$. − $C_{17}H_{17}N_6O_3RhS{\cdot}H_2O$ (506.4): calcd. C 40.33, H 3.78, N 16.60; found C 40.65, H 3.57, N 16.31.

Carbonyl(triphenylphosphane)[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), $TpmsRh(CO)PPh_3$ (5a): Triphenylphosphane (0.52 g, 2.0 mmol) was added to solution of **2a** (0.19 g, 0.40 mmol) in THF (200 mL). After 1 h, the solution was concentrated to a volume of 10 mL and overlaid with pentane. Crystallization yielded 0.29 g (100%) of a THF adduct of **5a** as bright-yellow needles. The crystals obtained were suitable for X-ray analysis. − ^1H NMR (200 MHz, CD_2Cl_2): δ = 6.38 (dd, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 2.2 Hz, 3 H, pyrazolyl 4-H), 7.29 (d, $^3J_{HH}$ = 2.2 Hz, 3 H, pyrazolyl 3-H), 7.5 [m, 15 H, $P(C_6H_5)_3$], 8.44 (d, $^3J_{HH}$ = 2.8 Hz, 3 H, pyrazolyl 5-H). − $^{31}P\{^1H\}$ NMR (200 MHz, CD_2Cl_2): δ = 45 (d, $^1J_{RhP}$ = 158 Hz). − $^{13}C\{^1H\}$ NMR (500 MHz, CD_2Cl_2): δ = 93.2 (s, C−SO_3), 106.4 (s, pyrazolyl C^4), 127.9 (d, $^2J_{PC}$ = 10 Hz, PPh_3 C^2), 129.9 (br. s, PPh_3 C^4), 130.5 (d, $^1J_{PC}$ = 3 Hz, PPh_3 C^1), 133.7 (d, $^3J_{PC}$ = 12 Hz, PPh_3 C^3), 134.7 (s, pyrazolyl C^5), 143.3 (s, pyrazolyl C^3), 187.3 (dd, $^1J_{RhC}$ = 74 Hz, $^2J_{PC}$ = 23 Hz, CO). − IR (KBr):

$\tilde{\nu}$ = 3168 cm^{-1}, 3154, 3134, 3124 (s, C−H), 1989 (vs, C=O), 1627 (s, C−C C_6H_5), 1520 (s, C=C), 1438 (s, P−C), 1479, 1438, 1405 (s, C−C C_6H_5), 1081, 1070, 1056, 1040 (s, S=O). − MS (FAB$^+$): *m/z* (%) = 686 (0.5) $[M]^+$, 658 (1.3) $[M - CO]^+$. − $(C_{29}H_{24}N_6O_4PRhS)_4(C_4H_8O)_3$ (2962.3): calcd. C 51.90, H 4.08, N 11.35; found C 51.98, H 4.12, N 11.22.

Carbonyl(trimethylphosphane)[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), TpmsRh(CO)PMe$_3$ (5b): A 1 M THF solution of trimethylphosphane (0.1 mL, 0.1 mmol) was slowly added to a solution of **2a** (45 mg, 0.10 mmol) in THF (50 mL). After 1 h, the solution was concentrated to a volume of 4 mL and overlaid with pentane. Crystallization yielded 56 mg (100%) of a THF adduct of **5b** as bright-yellow needles. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.48 [dd, $^3J_{RhH}$ = 10.3 Hz, $^2J_{PH}$ = 1.5 Hz, 9 H, $P(CH_3)_3$], 6.56 (dd, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 0.9 Hz, 3 H, pyrazolyl 4-H), 7.76 (d, $^3J_{HH}$ = 2.9 Hz, 3 H, pyrazolyl 3-H), 8.45 (br. s, 3 H, pyrazolyl 5-H). − ^{31}P{^{1}H} NMR (200 MHz, CD_2Cl_2): δ = 3 (d, $^1J_{RhP}$ = 148 Hz). − ^{13}C{^{1}H} (500 MHz, [D$_8$]THF): δ = 17.4 [d, $^1J_{PC}$ = 36.3 Hz, $P(CH_3)_3$], 107.2 (s, pyrazolyl C^4), 136.6 (s, pyrazolyl C^5), 144.0 (s, pyrazolyl C^3). − IR (KBr): $\tilde{\nu}$ = 3164 cm^{-1}, 3132 (s, C−H), 1990 (vs, C=O), 1519 (s, C=C), 1438 (s, P−C), 1081, 1068, 1057, 1044 (s, S=O). − MS (EI, 200 °C): *m/z* (%) = 500 (21.5) $[M]^+$, 472 (6.5) $[M - CO]^+$, 392 (19.9) $[M - CO - SO_3]^+$. − $(C_{14}H_{18}N_6O_4PRhS)\cdot(C_4H_8O)$ (560.4): calcd. C 37.77, H 4.58, N 14.68; found C 37.39, H 4.80, N 14.49.

Carbonyl(tricyclohexylphosphane)[tris(pyrazol-1-yl)methanesulfonato]rhodium(I), TpmsRh(CO)PCy$_3$ (5c): Tricyclohexylphosphane (0.14 g, 0.5 mmol) was added to solution of **2a** (45 mg, 0.10 mmol) in THF (50 mL). After 1 h, the solution was concentrated to a volume of 5 mL and overlaid with pentane. Crystallization yielded a bright-yellow THF adduct of **5c** (58 mg, 80%). − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1−2 [m, 33 H, $P(C_6H_{11})_3$], 6.54 (dd, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 0.7 Hz, 3 H, pyrazolyl 4-H), 7.78 (br. s, 3 H, pyrazolyl 3-H), 8.46 (br. s, 3 H, pyrazolyl 5-H). − ^{31}P{^{1}H} NMR (200 MHz, CD_2Cl_2): δ = 52 (d, $^1J_{RhP}$ = 153 Hz).[26] − IR (KBr): $\tilde{\nu}$ = 3168 cm^{-1} (vs, C−H), 2851, 2929 (vs, C−H), 1978 (vs,

Table 9. Crystallographic data for TpmsRh(CO)$_2$ (**2a**), TpmsRh(cod) (**3**), TpmsRh(nbd) (**4**), and TpmsRh(CO)PPh$_3$ (**5a**)

	2a	**3**	**4**	**5a**
Crystal shape	triclinic block	rod	plate	thin rod
Crystal colour	yellow	yellow	yellow	yellow
Crystal size [mm]	0.3 × 0.25 × 0.15	0.8 × 0.3 × 0.2	0.52 × 0.38 × 0.10	0.6 × 0.15 × 0.1
Empirical formula	$(C_{12}H_9N_6O_5RhS)_2\cdot(C_4H_8O)$	$C_{18}H_{21}N_6O_3RhS$	$C_{17}H_{17}N_6O_3RhS$	$(C_{29}H_{24}N_6O_4PRhS)\cdot(C_4H_8O)$
Molecular mass	488.27	504.38	488.34	758.59
Crystal system	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	*Pnma*	$P\bar{1}$
a [Å]	7.7753(1)	8.6948(1)	11.8020(9)	8.347(2)
b [Å]	10.7131(1)	14.6997(2)	9.7113(8)	14.353(2)
c [Å]	11.7510(2)	15.3120(1)	15.6993(12)	14.679(3)
α [°]	113.2735(9)	90	90	76.14(3)
β [°]	98.0074(9)	100.980(1)	90	82.12(4)
γ [°]	94.3890(4)	90	90	75.29(4)
V [Å^3]	881.05(2)	1921.21(3)	1799.3(2)	1646.0(6)
Z	2	4	4	2
$\rho_{calcd.}$ [g/cm^3]	1.841	1.744	1.803	1.531
Radiation used (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
T [K]	173(2)	173(2)	173(2)	173(2)
Scan method	φ scans	φ scans	φ scans	φ scans
μ [mm^{-1}]	1.132	1.032	1.099	0.682
Total reflections	8229	13914	13342	12681
Independent reflections	4694	5218	2815	7173
Unique reflections	3651	4343	2039	5115
Used reflections	4694	5218	2815	7173
R(int)	0.0295	0.0360	0.0459	0.0508
Scan range θ [°]	1.92−30.45	1.94−30.30	2.16−30.91	1.43−30.23
Index ranges	$-10 \le h \le 10$	$-11 \le h \le 12$	$-16 \le h \le 16$	$-11 \le h \le 11$
	$-14 \le k \le 14$	$-20 \le k \le 20$	$-10 \le k \le 13$	$-16 \le k \le 19$
	$-15 \le l \le 16$	$-12 \le l \le 21$	$-21 \le l \le 22$	$-20 \le l \le 18$
Completeness to $\theta_{max.}$ [%]	87.7	90.7	93.9	73.2
F(000)	488	1024	984	776
R,[a] wR^2 [$I > 2\sigma(I)$][b]	0.0335, 0.0729	0.0322, 0.0693	0.0336, 0.0717	0.0509, 0.0935
R indices (all data), *w*R^2	0.0513, 0.0805	0.0449, 0.0726	0.0593, 0.0817	0.0844, 0.1043
Maximum δ/σ	0.740	0.017	0.010	0.008
Max./min. el. density [e·Å^{-3}]	0.444/−0.611	0.677/−0.783	0.518/−0.663	1.043/−0.866
Used reflections	4694	5218	2815	7173
Least-squares restraints	5	0	0	0
Refined parameters	298	346	181	520
Goodness-of-fit on F^2 [c]	0.997	1.044	0.999	0.975
Weighting scheme parameters *a*/*b*[d]	0.0329/0	0.0311/0.4132	0.0321/2.4949	0.0410/0

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. − [b] $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)\}^{1/2}$. − [c] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}]$, *n* = number of reflections, *p* = parameters used. − [d] Definition of $w_{calcd.}$: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

C=O), 1520 (s, C=C), 1445 (s, P−C), 1081, 1067, 1054, 1041 (s, S=O). − MS (EI, 220 °C): *m/z* (%) = 704 (12.5) $[M]^+$, 676 (15.8) $[M - CO]^+$, 596 (5.6) $[M - CO - SO_3]^+$. − $(C_{29}H_{42}N_6O_4PRhS)_4 \cdot (C_4H_8O)$ (2890.7): calcd. C 49.86, H 6.14, N 11.63; found C 49.97, H 5.79, N 11.52.

Potassium Carbonyl[diphenyl(4-sulfonatophenyl)phosphane][tris(pyrazol-1-yl)methanesulfonato]rhodate(I), K[TpmsRh(CO)PPh$_2$-PhSO$_3$]·H$_2$O (5d): Potassium diphenyl(4-sulfonatophenyl)phosphane (0.1 g, 0.3 mmol) was added to a solution of **2a** (0.03 g, 0.06 mmol) in THF (10 mL). The vessel was pressurized with 3−4 atm of carbon monoxide and the mixture was stirred for 16 h at room temperature. The suspension obtained was then concentrated to half of its original volume and filtered. The filtrate was overlaid with pentane to yield 0.02 g of a yellow powder (40%). − ^{1}H NMR (200 MHz, D_3PO_4, D_2O): δ = 6.2 (br. s, 3 H, pyrazolyl 4-H), 6.8 (br. s, 3 H, pyrazolyl 3-/5-H), 7.3 [m, 14 H, P(C_6H_5)$_2$($C_6H_4SO_3K$)], 7.7 (br. s, 3 H, pyrazolyl 3-/5-H). − ^{31}P{^{1}H} NMR (200 MHz, D_3PO_4, D_2O): δ = 45 (d, $^1J_{RhP}$ = 159 Hz).[26] − IR (KBr): $\tilde{\nu}$ = 3167 cm^{-1}, 3058 (w, C−H), 1998 (vs, C=O), 1521 (s, C=C), 1436 (s, P−C), 1081, 1058, 1038 (s, S=O). − MS (FAB^+): *m/z* (%) = 805 (100.0) $[M + H]^+$, 776 (23.4) $[M - CO]^+$. − $C_{29}H_{23}KN_6O_7PS_2Rh \cdot H_2O$ (822.7): calcd. C 42.34, H 3.06, N 10.22; found C 42.80, H 3.34, N 9.63.

Crystal Structure Analyses: For all compounds **2a**, **3**, **4**, and **5a**, data were collected with a SMART 1K CCD area detector from Bruker AXS GmbH using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unless stated otherwise, data were collected at 173 K (Table 9). For protection against oxygen or moisture, single crystals were handled in a perfluoroalkyl ether from ABCR GmbH & Co KG (viscosity 1600 cSt). The unit cell was determined with the program SMART.[27] For data integration and refinement of the unit cell, the program SAINT[27] was used. The space group was determined using the programs XPREP[27] or ABSEN[28] and an empirical absorption correction was made using SADABS.[27] The structures were solved by direct methods using the programs SHELX-97[29] or SIR-97[30] and were refined by least-squares methods based on F^2 using SHELX-97.[29] Graphical representations of the molecular structures were generated using the program ZORTEP.[31] − The positions of disordered or non-refinable solvent molecules were calculated using the PLATON[32]-integrated SQUEEZE[33] procedure and the corresponding electron density was subtracted before the final refinement. − All non-hydrogen atoms were fully refined in the calculated positions; when possible, the hydrogen atoms were located from the electron density difference map and refined freely in both their positions and their thermal parameters. If a localization was not possible, the hydrogen atoms were positioned as a riding model on their neighbouring atoms and were refined depending on the positions of the latter. The figure in parentheses after each calculated value represents the standard deviation in units of the last significant digit. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151585−151588. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] S. Trofimenko, *J. Am. Chem. Soc.* **1966**, *88*, 1842.
[2] The nomenclature for tris(pyrazol-1-yl)borate ligands and their complexes, as proposed by Trofimenko,[3a] is used throughout this publication. Tp′ is used for Tp ligands with varying substituents.
[3] [3a] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943−980. − [3b] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**.
[4] [4a]N. F. Borkett, M. I. Bruce, *J. Organomet. Chem.* **1974**, *65*, C51. − [4b] D. J. O'Sullivan, F. J. Lalor, *J. Organomet. Chem.* **1974**, *65*, C47. − [4c] M. Cocivera, T. J. Desmond, G. Ferguson, B. Kaitner, F. J. Lalor, D. J. O'Sullivan, *Organometallics* **1982**, *1*, 1125−1132.
[5] W. Kläui, M. Berghahn, G. Rheinwald, H. Lang, *Angew. Chem.* **2000**, *112*, 2590−2592; *Angew. Chem. Int. Ed.* **2000**, *39*, 2464−2466.
[6] U. E. Bucher, A. Currao, R. Nesper, H. Rüegger, L. M. Venanzi, E.Younger, *Inorg. Chem.* **1995**, *34*, 66−74.
[7] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Anorganische Chemie*, 2nd ed., Walter de Gruyter, Berlin, **1995**.
[8] [8a] R. G. Ball, C. K. Gosh, J. K. Hoyano, A. D. McMaster, W. A. G. Graham, *J. Chem. Soc., Chem. Commun.* **1989**, 341−342. − [8b] M. Moszner, S. Wolowiec, A. Trösch, H. Vahrenkamp, *J. Organomet. Chem.* **2000**, *595*, 178−185. − [8c] E. Del Ministro, O. Renn, H. Rüegger, L. M. Venanzi, U. Burckhardt, V. Gramlich, *Inorg. Chim. Acta* **1995**, *240*, 631−639.
[9] [9a] H. V. R. Dias, H.-L. Lu, R. E. Ratcliff, S. G. Bott, *Inorg. Chem.* **1995**, *34*, 1975−1976. − [9b] H. V. R. Dias, J. D. Gorden, *Inorg. Chem.* **1996**, *35*, 318−324. − [9c] H. V. R. Dias, W. Jin, H.-J. Kim, H.-L. Lu, *Inorg. Chem.* **1996**, *35*, 2317−2328. − [9d] H. V. R. Dias, H.-J. Kim, H.-L. Lu, K. Rajeshwar, N. R. de Tacconi, A. Derecskei-Kovacs, D. S. Marynick, *Organometallics* **1996**, *15*, 2994−3003.
[10] A. L. Rheingold, B. S. Haggerty, G. P. A. Yap, S. Trofimenko, *Inorg. Chem.* **1997**, *36*, 5097−5103.
[11] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-oka, *Organometallics* **1997**, *16*, 4121−4128.
[12] D. Sanz, M. D. Santa María, R. M. Claramunt, M. Cano, J. V. Heras, J. A. Campo, F. A. Ruíz, E. Pinilla, A. Monge, *J. Organomet. Chem.* **1996**, *526*, 341−350.
[13] M. Cocivera, G. Ferguson, B. Kaitner, F. J. Lalor, D. J. O'Sullivan, M. Parvez, B. Ruhl, *Organometallics* **1982**, *1*, 1132−1139.
[14] T. P. E. Auf der Heyde, H.-B. Bürgi, *Inorg. Chem.* **1989**, *28*, 3970−3981.
[15] T. P. E. Auf der Heyde, H.-B. Bürgi, *Inorg. Chem.* **1989**, *28*, 3982−3989.
[16] M. Paneque, S. Sirol, M. Trujillo, E. Gutiérrez-Puebla, M. A. Monge, E. Carmona, *Angew. Chem.* **2000**, *112*, 224−227; *Angew. Chem. Int. Ed.* **2000**, *39*, 218−221.
[17] N. G. Connelly, D. J. H. Emslie, B. Metz, A. G. Orpen, M. J. Quayle, *Chem. Commun.* **1996**, 2289−2290.
[18] V. Chauby, C. S. Le Berre, P. Kalck, J.-C. Daran, G. Commenges, *Inorg. Chem.* **1996**, *35*, 6354−6355.
[19] B. Borak, A. M. Trzeciak, *VIth Regional Seminar of Ph.D. Students on Organometallic and Organophosphorus Chemistry*, Karpacz, Poland, **2000**.
[20] T. O. Northcutt, R. J. Lachicotte, W. D. Jones, *Organometallics* **1998**, *17*, 5148−5152.
[21] S. Juliá, J. M. del Mazo, L. Avila, J. Elguero, *Org. Prep. Proced. Int.* **1984**, *16(5)*, 299−307.
[22] J. A. McCleverty, G. Wilkinson, *Inorg. Synth.* **1967**, *8*, 211−214.
[23] E. W. Abel, M. A. Bennett, G. Wilkinson, *J. Chem. Soc.* **1959**, 3178−3182.
[24] J. Chatt, L. M. Venanzi, *J. Chem. Soc.* **1957**, 4735−4741.
[25] O. Herd, A. Heßler, K. P. Langhans, O. Stelzer, W. S. Sheldrick, N. Weferling, *J. Organomet. Chem.* **1994**, *475*, 99−111.
[26] Due to slow decarbonylation, a satisfactory ^{13}C{^{1}H} NMR spectrum could not be obtained.

[27] Bruker AXS Inc., Madison, WI, USA, **1998**.
[28] P. McArdle, *J. Appl. Crystallogr.* **1996**, *29*, 306.
[29] G. M. Sheldrick, *SHELX-97, Programs for Crystal Structure Analysis*, Release 97-2, University of Göttingen, Germany, **1997**.
[30] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115−119.
[31] L. Zsolnai, G. Huttner, University of Heidelberg, Germany, **1994**.
[32] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1999**.
[33] P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.
[34] These data were taken from the Cambridge Crystallographic Data Centre (CCDC).

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