

The Structure of $[\text{N}(\text{PPh}_3)_2][\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_8(\text{SCN})]$; Cation Dependent Structural Isomerism of the Anion

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Abstract

The X-ray structure of the $[\text{N}(\text{PPh}_3)_2]^+$ (PPN) salt of $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$ shows that the anion possesses the C_{3v} -like arrangement of CO ligands with three bridging COs around a triangular face, and with the SCN ligand occupying an axial site on that face. This contrasts with the previously determined structure of the $[\text{NMe}_2(\text{CH}_2\text{Ph})_2]^+$ salt of the anion which was shown to have the T_d -like all-terminal CO ligand arrangement. The presence of bridging carbonyl ligands leads to longer Ir–Ir bonds.

Introduction

The X-ray structure of the dimethyldibenzylammonium salt of the $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$ anion has recently been reported [1]. The structure of the anion was shown to have a T_d -like all-terminal CO ligand arrangement. However, it was also reported that in tetrahydrofuran solution, the same salt of the anion shows infrared absorptions due to bridging as well as terminal CO ligands [1]. In addition, it was found that the $[\text{NMe}_4]^+$ and $[\text{N}(\text{PPh}_3)_2]^+$ salts of $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$ showed, in their solid-state infrared spectra, typical absorptions due to bridging CO ligands.

In our studies of multidentate phosphine ligand substituted iridium clusters [2, 3] we have made use of the known reactivity of anionic iridium clusters to aid substitution reactions [4]. Our interest in the carbonyl ligand arrangements in these clusters [2] prompted us to determine the structure of the $[\text{N}(\text{PPh}_3)_2]^+$ salt of $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$, since this would allow a direct comparison between the T_d -like and C_{3v} -like structures of the anion in the solid state.

Results and Discussion

$[\text{N}(\text{PPh}_3)_2][\text{Ir}_4(\text{CO})_{11}(\text{SCN})]$ was prepared by refluxing a tetrahydrofuran suspension of $\text{Ir}_4(\text{CO})_{12}$

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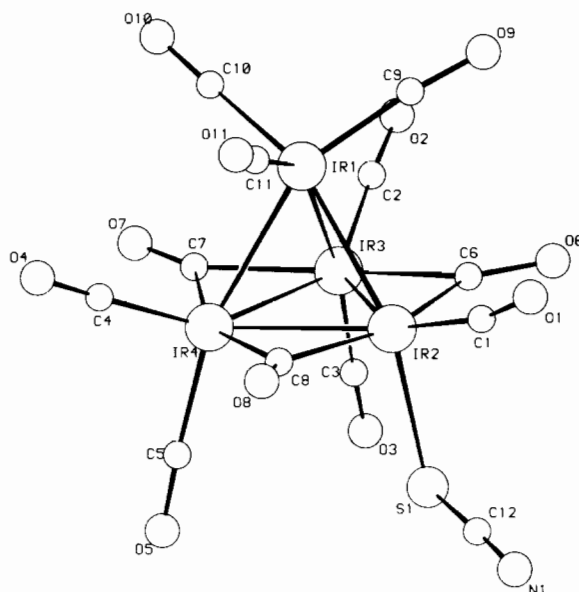


Fig. 1. The molecular structure of $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_8(\text{SCN})]^-$.

with $[\text{N}(\text{PPh}_3)_2]\text{SCN}$. Orange–yellow crystals of the product were obtained by slow evaporation of a dichloromethane/heptane solution of the complex under nitrogen. The molecular structure of the anion is shown in Fig. 1. Selected bond lengths and angles are given in Table 1, and atom parameters are given in Table 2. The molecule consists of a tetrahedron of iridium atoms, with three bridging carbonyl ligands around the basal plane. The SCN ligand occupies an axial coordination site on that basal plane. The SCN ligand is S-coordinated (Ir–S 2.422(9) Å), and is bent at the S atom (Ir–S–C 106.0(1.4)°). The orientation of the SCN ligand in this anion is significantly different to its orientation in the T_d -like anion of $[\text{NMe}_2(\text{CH}_2\text{Ph})_2][\text{Ir}_4(\text{CO})_{11}(\text{SCN})]$ [1]. The rotation of the SCN ligand by approximately 60° with respect to the basal plane of the metal tetrahedron to bring it into the same orientation as the T_d -like anion, causes close contacts with the $[\text{N}(\text{PPh}_3)_2]$ cation. Thus, the cations in the two crystals do not allow the same SCN orientation [5]. Also of interest is the comparison of

TABLE 1. Selected bond lengths (Å) and angles (°) in the anion $[\text{Ir}_4(\text{CO})_{11}\text{SCN}]^-$

Ir(1)	Ir(2)	2.696(2)	
Ir(1)	Ir(3)	2.700(2)	
Ir(1)	Ir(4)	2.703(2)	
Ir(2)	Ir(3)	2.735(2)	
Ir(2)	Ir(4)	2.724(2)	
Ir(3)	Ir(4)	2.703(2)	
Ir(2)	S(1)	2.422(9)	
S(1)	C(12)	1.58(4)	
C(12)	N(1)	1.09(6)	
Ir(2)	C(1)	1.88(3)	
Ir(3)	C(2)	1.80(3)	
Ir(3)	C(3)	1.93(3)	
Ir(4)	C(4)	1.84(3)	
Ir(4)	C(5)	1.91(4)	
Ir(2)	C(6)	1.94(3)	
Ir(3)	C(6)	2.16(3)	
Ir(3)	C(7)	2.09(4)	
Ir(4)	C(7)	2.20(4)	
Ir(2)	C(8)	2.10(3)	
Ir(4)	C(8)	2.25(3)	
Ir(1)	C(9)	1.90(3)	
Ir(1)	C(10)	1.96(3)	
Ir(1)	C(11)	1.99(4)	
C(1)	O(1)	1.10(4)	
C(2)	O(2)	1.18(4)	
C(3)	O(3)	1.11(4)	
C(4)	O(4)	1.15(4)	
C(5)	O(5)	1.19(4)	
C(6)	O(6)	1.27(4)	
C(7)	O(7)	1.11(5)	
C(8)	O(8)	1.12(4)	
C(9)	O(9)	1.20(4)	
C(10)	O(10)	1.14(4)	
C(11)	O(11)	1.08(4)	
Ir(1)	Ir(2)	S(1)	153.1(2)
Ir(3)	Ir(2)	S(1)	96.5(2)
Ir(4)	Ir(2)	S(1)	98.4(2)
Ir(2)	S(1)	C(12)	106.0(14)
S(1)	C(12)	N(1)	172.2(38)
Ir(2)	C(6)	Ir(3)	83.5(12)
Ir(2)	C(6)	O(6)	141.0(24)
Ir(3)	C(6)	O(6)	134.9(23)
Ir(3)	C(7)	Ir(4)	78.0(13)
Ir(3)	C(7)	O(7)	146.3(32)
Ir(4)	C(7)	O(7)	135.4(30)
Ir(2)	C(8)	Ir(4)	77.3(10)
Ir(2)	C(8)	O(8)	142.0(26)
Ir(4)	C(8)	O(8)	140.5(26)

the metal–metal bond distances in this anion with those of the previously reported T_d -like structure of the $[\text{NMe}_2(\text{CH}_2\text{Ph})_2]^+$ salt [1]. In the all-terminal CO T_d -like structure the average Ir–Ir distance is 2.684(1) Å (range 2.656–2.698 Å). In the bridged CO C_{3v} -like structure the average non-bridged Ir–Ir distance is 2.700(2) Å and the average bridged Ir–Ir distance is 2.721(2) Å. This provides further clear

TABLE 2. Fractional coordinates for $[(\text{C}_6\text{H}_5)_3\text{PNP}(\text{C}_6\text{H}_5)_3]^- [\text{Ir}_4(\text{CO})_{11}\text{SCN}]$

	x	y	z
Ir(1)	0.0493(1)	0.0197(1)	0.1849(1)
Ir(2)	−0.0864(1)	0.0899(1)	0.2099(1)
Ir(3)	0.0446(1)	0.1384(1)	0.2721(1)
Ir(4)	−0.0316(1)	0.0307(1)	0.3518(1)
S(1)	−0.1793(5)	0.1668(4)	0.2924(7)
C(12)	−0.2596(21)	0.1564(17)	0.2545(26)
N(1)	−0.3173(23)	0.1560(22)	0.2322(29)
P(1)	0.5674(4)	0.1776(4)	0.7520(6)
P(2)	0.4884(4)	0.0488(4)	0.7389(6)
N(2)	0.5573(12)	0.1058(11)	0.7173(18)
C(1)	−0.1399(17)	0.0804(15)	0.1099(24)
C(2)	0.1394(19)	0.1675(16)	0.2191(25)
C(3)	0.0130(16)	0.2132(16)	0.3503(24)
C(4)	−0.0202(17)	−0.0560(17)	0.3902(25)
C(5)	−0.1059(18)	0.0548(16)	0.4533(77)
C(6)	−0.0165(16)	0.1609(15)	0.1599(24)
C(7)	0.0789(21)	0.0792(18)	0.3747(29)
C(8)	−0.1318(17)	0.0027(16)	0.2772(23)
C(9)	0.0850(16)	0.0535(15)	0.0681(25)
C(10)	0.1477(18)	−0.0134(16)	0.2201(25)
C(11)	−0.0009(19)	−0.0685(18)	0.1685(27)
O(1)	−0.1586(16)	0.0700(14)	0.0446(21)
O(2)	0.1998(14)	0.1897(11)	0.1842(19)
O(3)	−0.0048(18)	0.2576(13)	0.3931(23)
O(4)	−0.0191(15)	−0.1126(13)	0.4058(18)
O(5)	−0.1422(14)	0.0805(13)	0.5174(18)
O(6)	−0.0103(11)	0.2059(9)	0.0994(15)
O(7)	0.1255(13)	0.0683(11)	0.4170(17)
O(8)	−0.1771(12)	−0.0375(10)	0.2753(17)
O(9)	0.1040(13)	0.0816(11)	−0.0021(16)
O(10)	0.2050(12)	−0.0324(11)	0.2406(19)
O(11)	−0.0287(13)	−0.1151(10)	0.1543(15)
C(30)	0.6388(11)	0.1193(8)	0.8831(14)
C(31)	0.6719(11)	0.1173(8)	0.9624(14)
C(32)	0.6791(11)	0.1762(8)	1.0107(14)
C(33)	0.6533(11)	0.2372(8)	0.9796(14)
C(34)	0.6202(11)	0.2391(8)	0.9002(14)
C(35)	0.6130(11)	0.1802(8)	0.8520(14)
C(40)	0.4373(13)	0.2361(10)	0.8648(13)
C(41)	0.3675(13)	0.2731(10)	0.8754(13)
C(42)	0.3382(13)	0.2984(10)	0.8004(13)
C(43)	0.3787(13)	0.2867(10)	0.7147(13)
C(44)	0.4484(13)	0.2497(10)	0.7041(13)
C(45)	0.4777(13)	0.2244(10)	0.7791(13)
C(50)	0.6665(12)	0.1802(8)	0.5910(16)
C(51)	0.7170(12)	0.2121(8)	0.5231(16)
C(52)	0.7351(12)	0.2799(8)	0.5311(16)
C(53)	0.7027(12)	0.3159(8)	0.6070(16)
C(54)	0.6522(12)	0.2840(8)	0.6748(16)
C(55)	0.6341(12)	0.2161(8)	0.6668(16)
C(60)	0.4395(9)	0.0584(10)	0.9183(15)
C(61)	0.3858(9)	0.0713(10)	0.9949(15)
C(62)	0.3093(9)	0.0916(10)	0.9869(15)
C(63)	0.2865(9)	0.0988(10)	0.9021(15)
C(64)	0.3403(9)	0.0859(10)	0.8255(15)
C(65)	0.4167(9)	0.0657(10)	0.8355(15)

(continued)

TABLE 2. (continued)

	x	y	z
C(70)	0.3833(11)	-0.0142(8)	0.6405(13)
C(71)	0.3383(11)	-0.0173(8)	0.5705(13)
C(72)	0.3493(11)	0.0303(8)	0.5018(13)
C(73)	0.4053(11)	0.0809(8)	0.5032(13)
C(74)	0.4503(11)	0.0839(8)	0.5731(13)
C(75)	0.4394(11)	0.0364(8)	0.6418(13)
C(80)	0.6187(10)	-0.0329(8)	0.7344(13)
C(81)	0.6560(10)	-0.0945(8)	0.7414(13)
C(82)	0.6120(10)	-0.1507(8)	0.7730(13)
C(83)	0.5307(10)	-0.1453(8)	0.7976(13)
C(84)	0.4935(10)	-0.0837(8)	0.7905(13)
C(85)	0.5375(10)	-0.0274(8)	0.7589(13)

evidence for the recently reported [6] observation that CO bridged Ir–Ir bonds are longer than non-bridged Ir–Ir bonds.

A comparison of Ir–C and C–O distances in the two $[Ir_4(CO)_{11}(SCN)]^-$ structures is not justified in view of the large estimated standard deviations in the distances concerned.

The variation in ligand conformation of a metal carbonyl cluster with changes in the counterion has been observed previously in the case of $[Fe(py)_6]^{2+}$ and $[N(PPh_3)_2]^+$ salts of the $[Fe_4(CO)_{13}]^{2-}$ anion, where a change from a semi-bridging to a non-bridging conformation is observed [7]. Clearly in that case, and in the case of the $[Ir_4(CO)_{11}(SCN)]^-$ anion reported in this paper, very minor effects are responsible for changing the CO ligand conformation, with the energy difference between the two conformations necessarily being very small.

Experimental

Preparation of $[N(PPh_3)_2][Ir_4(CO)_{11}(SCN)]$

All operations were carried out under a nitrogen atmosphere. A mixture of $Ir_4(CO)_{12}$ (0.042 g, 0.038 mmol) and $[N(PPh_3)_2]SCN$ (0.068 g, 0.11 mmol) in thf (25 cm³) was refluxed for 4 h. The solution was then evaporated to dryness, the residue was washed with water, and the product recrystallised from dichloromethane/heptane (0.057 g, 0.034 mmol). Infrared (CH₂Cl₂ solution): 2106w, 2080w, 2045vs, 2020sh, 2005s, 1819m.

Determination of Crystal Structure

Orange crystals were isolated from dichloromethane–heptane solution.

Crystal Data

$C_{48}H_{30}Ir_4N_2O_{11}F_2S$, molecular weight = 1673.60, monoclinic, $a = 17.163(10)$, $b = 19.910(10)$, $c = 15.066(9)$ Å, $\beta = 81.77(2)^\circ$, $V = 5095.3$ Å³, space

group $P2_1/a$ (determined from Weissenberg photographs), $Z = 4$, $D_c = 2.18$ g cm⁻³. Crystal dimensions were $c. 0.3 \times 0.3 \times 0.18$ mm, $\mu(Mo K\alpha) = 111.56$ cm⁻¹.

Data Collection and Processing

Stoe STADI-2 two-circle diffractometer, graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å); 6957 reflections measured ($5 \leq 2\theta \leq 45^\circ$), 6186 unique.

Structure Analysis and Refinement

The structure was solved by Patterson (SHELX86) [8] and Fourier (SHELX76) [9] methods. Empirical corrections for absorption were made using the program DIFABS [10]. Atoms other than carbon and hydrogen were treated anisotropically and the carbon atom of the SCN group was also treated anisotropically. The intensity data was not of sufficient quality to give satisfactory results when the carbon atoms were treated anisotropically. The carbon atoms of the benzene rings were constrained to D_{6h} symmetry and the C–C bond lengths to 1.395 Å. The hydrogen atoms were placed in idealised positions (C–H 1.08 Å) with $U = 0.050$ Å². Final stages of refinement were by full matrix least-squares methods to give $R = 0.067$, $R_w = 0.064$ for 3463 reflections with $F > 6\sigma(F)$ and the weighting scheme was $w = 1/(\sigma^2(F) + 0.000416F^2)$. The final electron-density difference map showed peaks of $c. 1.21$ (maximum) and -1.24 (minimum) e Å⁻³.

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References

- 1 R. Della Pergola, L. Garlaschelli, S. Martinengo, F. Demartin, M. Manassero and M. Sansoni, *Gazz. Chim. Ital.*, **117** (1987) 245.
- 2 J. A. Clucas, M. M. Harding, B. S. Nicholls and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, (1984) 319.
- 3 M. M. Harding, B. S. Nicholls and A. K. Smith, *Acta Crystallogr., Sect. C*, **39** (1984) 790.
- 4 R. Ros, A. Scriveranti, V. G. Albano, D. Braga and L. Garlaschelli, *J. Chem. Soc., Dalton Trans.*, (1986) 2411.
- 5 D. Braga, personal communication.
- 6 D. Braga and F. Grepioni, *J. Organomet. Chem.*, **336** (1987) C9.
- 7 G. van Buskirk, C. B. Knobler and H. D. Kesz, *Organometallics*, **4** (1985) 149.
- 8 G. M. Sheldrick, *SHELX86*, program for crystal structure solution, University of Göttingen, F.R.G., 1986.
- 9 G. M. Sheldrick, *SHELX76*, program for crystal structure determination, University of Cambridge, U.K., 1976.
- 10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.