Inorganica Chimica Acta, *161* (1989) 239–245

On the Non-isostructures of $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr)

LING-KANG LIU*, JIANN-T'SUEN LIN* and DUENCHENG FANG
Institute of Chemistry, Academia Sinica, Nankang, Taipei 11529 (Taiwan)

(Received November 23, 1988; revised February 13, 1989)

Abstract

$M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr) have been found seemingly isomorphous but non-isostructural in the crystalline state. Both W and Cr complexes have been found to crystallize in the orthorhombic space group *Pna*2_1. A combination of thermal parameter and bond length considerations has led to the conclusion that $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ has the *cis*-CO–CO, *cis*-CH_3CN–CH_3CN and *cis*-NO–$Sn(C_6H_5)_3$ configuration, whereas $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ has the *cis*-CO–CO, *cis*-CH_3CN–CH_3CN and *trans*-NO–$Sn(C_6H_5)_3$ configuration.

Introduction

A linearly coordinated NO group has been considered to be a fairly good π-acid and sometimes even better than a CO group. With the dual bonding modes of NO, facile ligand substitution reactions have been reported for metal–NO complexes [1]. Recently we were able to successfully synthesize *trans*-$M(CO)_4(NO)(Sn(C_6H_5)_3)$ (M = W, Cr) whose exceedingly high CO stretching frequencies suggested the possibility of nucleophilic attack at CO, i.e. by the O atom of $(CH_3)_3NO$ to generate coordinative unsaturation after elimination of CO_2 and $(CH_3)_3N$ [2]. In CH_3CN medium, the CH_3CN molecules would then occupy the vacant site(s) eventually leading to (CH_3CN)–metal bond formation. The reaction of *trans*-$M(CO)_4(NO)(Sn(C_6H_5)_3)$ with 2 equivalents of $(CH_3)_3NO$ in CH_3CN, therefore, resulted in $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ in moderate yields [3]. A *cis*-CO–CO assignment was ascertained by the infrared spectra. The proton NMR (in CD_3CN), however, consisted of 2 coordinated CH_3CN peaks for $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ but only 1 such peak for $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$.

There have been two rationalizations: (a) a difference in their molecular structures and/or (b) a fast exchange behaviour of CH_3CN only for $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ but not for $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$. The resolution has been accomplished via this X-ray crystallographic study.

Experimental

The synthesis of $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr) was detailed elsewhere [3]. The crystals suitable for X-ray structure analysis were obtained from cold ether/hexane. The X-ray diffraction experiments are summarized in Table 1 from which the crystals of $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr) are seen likely to be isomorphous. The first idea was that they belonged to the centric space group *Pnam*, a non-standard setting for *Pnma* [4]. Though the heavier atoms could be located, the refinements did not go anywhere. After switching to the non-centric *Pna*2_1, the structures refined smoothly. As *Pna*2_1 is a polar space group, the chirality was assigned based on the results from the anomalous dispersion of heavier atoms [5]. The ambiguities of locating the NO and CO positions [6] were solved according to the chemical/crystallographical meaningfulness of thermal parameters. For models A, B, and C as defined in Fig. 1, the more restricted N/C should conform to a lower U than neighboring O. Parallel sets of least-squares refinement were performed until convergence as detailed in Table 2. Model C for the W structure was judged to be correct on the basis of thermal parameter considerations. For the Cr structure, the Cr–N(NO) showed a shorter bond length than Cr–C(CO) by *c.* 0.2 Å in model A but Cr–N(NO) showed an even longer bond length than the Cr–C(CO) bond length in model C. Hence model A for the Cr structure was judged to be correct. The atomic scattering factors f' and f'' were taken from the International Tables [5]. All hydrogen atoms were calculated after the anisotropic convergence and included isotropically without refining. The calculations employed a VAX-780 computer using the NRCC package [7]. Final fractional coordinates of $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ are in the (x, y, z) set and those of $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ are in the ($1 - x$, $1 - y$, $1 - z$) set (Tables

---

*Authors to whom correspondence should be addressed.

0020-1693/89/$3.50

TABLE 1. Summary of experimental data and structure refinement parameters for $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr)

	M = W	M = Cr
Empirical formula	$C_{24}H_{21}N_3O_3SnW$	$C_{24}H_{21}CrN_3O_3Sn$
Formula weight	701.74	569.93
Crystal system	orthorhombic	orthorhombic
Space group	$Pna2_1$	$Pna2_1$
Lattice constants		
a (Å)	13.311(6)	13.046(2)
b (Å)	12.194(4)	12.159(2)
c (Å)	15.278(5)	15.353(3)
V (Å^3)	2479.77	2435.50
Z	4	4
F(000)	1335.64	1135.81
D_{calc} (Mg/m^3)	1.880	1.555
Temperature (K)	298	298
Radiation	Mo Kα	Mo Kα
Wavelength, λ (Å)	0.7093	0.7093
Absorption coefficient μ (mm^{-1})	5.77	1.49
Crystal dimensions (mm)	0.20 × 0.20 × 0.35	0.30 × 0.40 × 0.40
No. reflections used for lattice constants	25	25
2θ angle range (°)	10–20	14–22
Diffractometer	Nonius CAD-4 with graphite monochromator	
Scan method	$\theta-2\theta$ scan	
Scan width	$2(0.7 + 3.5 \tan\theta)$	$2(0.7 + 3.5 \tan\theta)$
2θ range (°)	2–60	2–60
Range of hkl	−18,−17,−21 to 0,0,0	−18,−17,−21 to 0,0,0
Standard reflections	(10,0,0) (0,6,0) (0,0,8)	(−2,−6,−4) (−2,−6,4) (2,6,4)
Recollection time (s)	7200	7200
Intensity decay (%)	2	6
Min. transmission	0.7959	0.9397
Max. transmission	0.9998	0.9777
Correction for intensity decay	no	yes
Correction for absorption	yes	yes
No reflections measured	3736	3666
No reflections observed ($I > 2.5\sigma(I)$)	2534	1780
Structure solution	Patterson and Fourier methods	
Structure refinement	full-matrix least-squares	
No. atoms	53	53
No. parameters	288	288
Quantity minimized	sum $(w(F_o - F_c)^2)$	
Weights	counting-statistics only	
R	0.025	0.029
R_w	0.016	0.019
Goodness of fit	1.395	1.311
Max. Δ/σ	0.001	0.045
Final difference map		
Deepest hole (e/Å^3)	−0.340	−0.780
Highest peak (e/Å^3)	0.320	0.650

3 and 4, respectively). The molecular drawings [8] for both molecules are given in Fig. 2 with the structural parameters listed in Tables 5 and 6 for the W structure and the Cr structure, respectively.

These descriptions could not be based on a space group of unnecessarily low symmetry [9], i.e. *Pnam* cannot be the 'correct' space group in the crystalline state. Neither the W structure nor the Cr structure was found to have an approximate mirror to be placed perpendicular to the crystallographic z axis. Both structures could not refine in the space group *Pnma*, either.

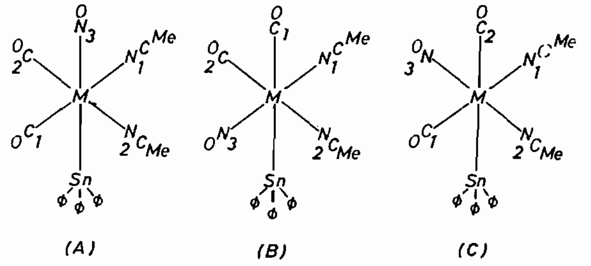

Fig. 1. The models relevant to structure analysis reported here. Model B and model C are chemically equivalent: both have the NO ligand *trans* to one of the CH_3CN ligands. Nonetheless, they are so drawn to emphasize their crystallographic difference.

Results and Discussion

For these bis-acetonitrile complexes, no unambiguous CN stretching bands could be found. Two intense CO and one NO stretching bands were consistent with the *cis*-CO–CO configuration (Table 7). A decrease by about 100 cm^{-1} relative to their parent complexes could be reasoned by the impotence of CH_3CN to function as a π-acceptor. The X-ray structures have confirmed the formulation that two labile CH_3CN ligands have replaced two CO ligands. The geometry of the coordination core about W and Cr is approximately octahedral.

TABLE 2. Results of the models used in parallel least-squares refinement for $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ (M = W, Cr)

	M = W[a]			M = Cr[b]		
	A	B	C	A	B	C
Correct chirality						
U(C1)	0.051(3)	0.058(4)	0.050(3)	0.059(4)	0.052(4)	0.060(4)
U(O1)	0.075(3)	0.092(4)	0.075(3)	0.075(4)	0.086(3)	0.075(3)
U(C2)	0.046(3)	0.046(3)	0.057(4)	0.052(4)	0.039(3)	0.040(3)
U(O2)	0.088(4)	0.090(4)	0.091(4)	0.085(4)	0.081(4)	0.081(4)
U(N3)	0.108(5)	0.087(4)	0.078(4)	0.070(4)	0.103(5)	0.084(5)
U(O3)	0.093(4)	0.077(3)	0.090(4)	0.085(4)	0.078(4)	0.089(4)
R	0.035	0.035	0.035	0.048	0.049	0.048
R_w	0.027	0.027	0.026	0.039	0.41	0.039
GOF	2.30	2.30	2.26	2.55	2.66	2.55
The other chirality						
U(C1)	0.046(4)	0.066(5)	0.046(4)	0.060(4)	0.053(4)	0.061(4)
U(O1)	0.074(4)	0.091(4)	0.075(4)	0.078(4)	0.085(4)	0.077(4)
U(C2)	0.044(4)	0.043(4)	0.064(5)	0.053(4)	0.039(3)	0.039(3)
U(O2)	0.092(5)	0.093(5)	0.091(4)	0.083(4)	0.080(4)	0.079(4)
U(N3)	0.119(7)	0.078(5)	0.073(5)	0.069(4)	0.105(6)	0.086(5)
U(O3)	0.093(4)	0.077(4)	0.092(5)	0.083(4)	0.081(4)	0.087(4)
R	0.042	0.042	0.041	0.049	0.051	0.049
R_w	0.033	0.033	0.032	0.040	0.042	0.040
GOF	2.81	2.79	2.73	2.58	2.70	2.58
Final refinement						
U(C1)			0.049(4)	0.052(4)		
U(O1)			0.077(3)	0.076(4)		
U(C2)			0.056(4)	0.053(4)		
U(O2)			0.102(4)	0.084(4)		
U(N3)			0.070(4)	0.061(3)		
U(O3)			0.095(4)	0.087(4)		
R			0.025	0.029		
R_w			0.016	0.019		
GOF			1.395	1.311		

[a] For models, 2534 reflections, 128 variables, 32 non-hydrogen atoms; for final, 32 anisotropic non-hydrogen atoms plus 21 fixed hydrogen atoms. [b] Same as in a except for 1780 reflections.

TABLE 3. Final fractional coordinates of non-hydrogen atoms for $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$

Atom	x	y	z	B_{iso}
W	0.48049(2)	0.60346(2)	0.24575(5)	3.485(13)
Sn	0.66407(3)	0.50127(5)	0.20495	3.215(19)
O1	0.5532(4)	0.8103(5)	0.1482(4)	6.1(3)
O2	0.2734(4)	0.6982(5)	0.2932(5)	8.1(4)
O3	0.4044(5)	0.5200(6)	0.0685(5)	7.5(4)
N1	0.4546(5)	0.4574(5)	0.3211(5)	4.3(3)
N2	0.5528(5)	0.6602(6)	0.3634(5)	4.7(4)
N3	0.4330(5)	0.5495(6)	0.1376(5)	5.5(4)
C1	0.5238(5)	0.7348(6)	0.1865(5)	3.9(4)
C2	0.3535(6)	0.6636(6)	0.2766(6)	4.4(4)
C3	0.4257(6)	0.2797(9)	0.4111(7)	7.0(6)
C4	0.4418(6)	0.3784(7)	0.3618(6)	4.4(4)
C5	0.6614(9)	0.7209(8)	0.4941(6)	8.1(7)
C6	0.5977(7)	0.6868(8)	0.4211(6)	5.4(5)
C11	0.7388(5)	0.5558(7)	0.0860(5)	3.2(4)
C12	0.7832(6)	0.6607(7)	0.0842(5)	4.0(4)
C13	0.8264(6)	0.6974(7)	0.0082(6)	4.5(4)
C14	0.8271(6)	0.6362(8)	−0.0664(5)	4.7(5)
C15	0.7820(6)	0.5354(8)	−0.0644(6)	4.4(4)
C16	0.7370(6)	0.4949(7)	0.0113(6)	3.6(4)
C21	0.6514(5)	0.3253(6)	0.1892(5)	3.3(3)
C22	0.7311(5)	0.2561(7)	0.2038(5)	4.5(4)
C23	0.7212(7)	0.1444(7)	0.1967(6)	5.3(5)
C24	0.6325(8)	0.0976(7)	0.1790(6)	5.9(5)
C25	0.5520(7)	0.1617(8)	0.1645(7)	6.3(5)
C26	0.5613(6)	0.2752(7)	0.1693(7)	5.7(5)
C31	0.7808(6)	0.5066(7)	0.3043(5)	3.8(4)
C32	0.8793(6)	0.5397(7)	0.2877(6)	4.5(4)
C33	0.9507(6)	0.5423(8)	0.3521(7)	5.8(5)
C34	0.9250(7)	0.5124(8)	0.4349(7)	6.0(5)
C35	0.8296(8)	0.4802(9)	0.4549(6)	6.1(6)
C36	0.7595(7)	0.4766(8)	0.3892(6)	4.8(5)

TABLE 4. Final fractional coordinates of non-hydrogen atoms for $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$

Atom	x	y	z	B_{iso}
Cr	0.52394(9)	0.39825(10)	0.74636(11)	3.71(5)
Sn	0.34420(3)	0.49806(5)	0.79340	3.38(2)
O1	0.4444(5)	0.2039(4)	0.8473(4)	6.0(4)
O2	0.5829(5)	0.4799(6)	0.9218(5)	6.6(4)
O3	0.7260(4)	0.3107(5)	0.7228(5)	7.0(4)
N1	0.5447(5)	0.5405(6)	0.6784(5)	4.1(3)
N2	0.4488(5)	0.3460(5)	0.6378(5)	4.5(4)
N3	0.6410(5)	0.3452(5)	0.7274(5)	4.8(3)
C1	0.4729(6)	0.2761(7)	0.8069(6)	4.1(4)
C2	0.5621(7)	0.4549(7)	0.8541(6)	4.2(4)
C3	0.5764(6)	0.7222(8)	0.5939(7)	6.3(5)
C4	0.5585(6)	0.6184(8)	0.6400(6)	4.5(4)
C5	0.3344(10)	0.2777(7)	0.5113(7)	7.7(6)
C6	0.3994(7)	0.3157(7)	0.5822(6)	5.0(5)
C11	0.2677(6)	0.4469(6)	0.9103(6)	3.6(4)
C12	0.2697(7)	0.5070(8)	0.9856(8)	3.9(4)
C13	0.2215(7)	0.4732(8)	1.0608(6)	4.6(5)
C14	0.1723(7)	0.3743(8)	1.0636(5)	5.2(5)
C15	0.1714(7)	0.3113(7)	0.9910(6)	5.2(5)
C16	0.2186(6)	0.3450(7)	0.9152(5)	3.9(4)
C21	0.3591(6)	0.6748(5)	0.8102(5)	3.5(3)
C22	0.4501(7)	0.7267(7)	0.8293(7)	6.0(6)
C23	0.4581(8)	0.8379(8)	0.8348(7)	6.9(6)
C24	0.3747(8)	0.9019(7)	0.8189(6)	6.2(6)
C25	0.2843(7)	0.8569(7)	0.8011(8)	5.1(5)
C26	0.2761(5)	0.7416(6)	0.7942(7)	4.6(5)
C31	0.2276(6)	0.4918(7)	0.6947(5)	3.7(4)
C32	0.2502(8)	0.5292(8)	0.6119(8)	4.7(5)
C33	0.1779(8)	0.5245(9)	0.5440(6)	6.0(6)
C34	0.0807(7)	0.4867(9)	0.5603(6)	5.8(5)
C35	0.0576(7)	0.4537(7)	0.6421(7)	5.6(5)
C36	0.1296(6)	0.4557(6)	0.7086(5)	4.3(4)

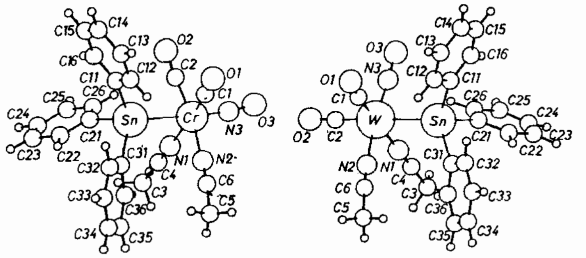

Fig. 2. ORTEP drawings for $M(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$, M = Cr and W. The NO ligands have been darkened for easy differentiation. Atomic numbering sequences are attached. The W compound has a chiral center but not the Cr compound.

$W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ is seen in Fig. 2 to have the *cis*-CO–CO, *cis*-CH_3CN–CH_3CN and *cis*-NO–$Sn(C_6H_5)_3$ configuration but $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ shows the *cis*-CO–CO, *cis*-CH_3CN–CH_3CN and *trans*-NO–$Sn(C_6H_5)_3$ configuration. The proton NMR spectrum of $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ shows two peaks with the same intensity at 2.15 and 2.08 ppm in the acetonitrile CH_3 region, attributable to the two different coordinated CH_3CN ligands. That of $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$ shows only one peak at 1.98 ppm, the same as that of free CH_3CN – a fast exchange between free CH_3CN and coordinated CH_3CN on the time scale of NMR spectroscopy (*c.* 10^{-9} s), or the coordinated CH_3CN on Cr has had the same chemical shift as that of free CH_3CN. In view of the crystal structure, there is to be a local mirror passing Cr and bisecting the two CH_3CN ligands when free rotation around the Cr–Sn bond is possible. If the X-ray structure of the Cr complex is considered a minimum energy state to be kept in the solution, the two CH_3CN ligands are equivalent in the proton NMR spectrum. For the Cr structure the fast exchange cannot be ruled out, nonetheless.

With NO *trans* to $Sn(C_6H_5)_3$ in the Cr structure, Cr–N(NO) is shorter than Cr–N(CH_3CN) by *c.* 0.35 Å. On the other hand, with NO *cis* to $Sn(C_6H_5)_3$ and *trans* to CH_3CN in the W structure, such a

TABLE 5. Bond lengths and bond angles involving non-hydrogen atoms for $W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$, *Pna*$2_1$

W–Sn	2.813(1)	N1–C4	1.159(11)	C21–C26	1.380(11)
W–N1	2.149(7)	N2–C6	1.113(13)	C22–C23	1.373(12)
W–N2	2.154(8)	C3–C4	1.435(13)	C23–C24	1.340(14)
W–N3	1.888(8)	C5–C6	1.461(14)	C24–C25	1.345(15)
W–C1	1.928(8)	C11–C12	1.410(11)	C25–C26	1.392(13)
W–C2	1.902(8)	C11–C16	1.362(12)	C31–C32	1.395(11)
Sn–C11	2.175(8)	C12–C13	1.371(12)	C31–C36	1.377(13)
Sn–C21	2.166(7)	C13–C14	1.362(13)	C32–C33	1.368(13)
Sn–C31	2.172(8)	C14–C15	1.367(14)	C33–C34	1.360(16)
O1–C1	1.159(10)	C15–C16	1.394(13)	C34–C35	1.363(15)
O2–C2	1.174(10)	C21–C22	1.374(11)	C35–C36	1.372(13)
O3–N3	1.178(11)				
Sn–W–N1	83.7(2)	N1–C4–C3	179.3(10)		
Sn–W–N2	86.5(2)	N2–C6–C5	176.9(11)		
Sn–W–N3	86.7(2)	Sn–C11–C12	119.0(6)		
Sn–W–C1	90.3(2)	Sn–C11–C16	121.7(6)		
Sn–W–C2	176.2(2)	C12–C11–C16	119.1(8)		
N1–W–N2	83.7(3)	C11–C12–C13	119.3(7)		
N1–W–N3	97.2(3)	C12–C13–C14	122.2(8)		
N1–W–C1	171.2(3)	C13–C14–C15	118.0(8)		
N1–W–C2	92.5(3)	C14–C15–C16	121.8(8)		
N2–W–N3	173.0(3)	C11–C16–C15	119.6(8)		
N2–W–C1	89.5(3)	Sn–C21–C22	122.0(6)		
N2–W–C2	93.8(3)	Sn–C21–C26	122.1(5)		
N3–W–C1	88.8(3)	C22–C21–C26	115.8(7)		
N3–W–C2	93.1(3)	C21–C22–C23	121.5(7)		
C1–W–C2	93.5(3)	C22–C23–C24	121.6(8)		
W–Sn–C11	116.6(2)	C23–C24–C25	119.2(8)		
W–Sn–C21	113.3(2)	C24–C25–C26	119.9(8)		
W–Sn–C31	116.9(2)	C21–C26–C25	122.0(8)		
C11–Sn–C21	104.2(3)	Sn–C31–C32	123.7(6)		
C11–Sn–C31	104.3(3)	Sn–C31–C36	120.2(6)		
C21–Sn–C31	99.4(3)	C32–C31–C36	116.1(7)		
W–N1–C4	179.2(6)	C31–C32–C33	121.9(8)		
W–N2–C6	174.1(7)	C32–C33–C34	119.2(8)		
W–N3–O3	177.2(7)	C33–C34–C35	121.3(9)		
W–C1–O1	176.3(7)	C34–C35–C36	118.6(9)		
W–C2–O2	177.4(8)	C31–C36–C35	122.8(9)		

TABLE 6. Bond lengths and bond angles involving non-hydrogen atoms for $Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$, *Pna*$2_1$

Cr–Sn	2.7373(13)	N1–C4	1.130(12)	C21–C26	1.376(10)
Cr–N1	2.038(7)	N2–C6	1.132(12)	C22–C23	1.359(13)
Cr–N2	2.036(7)	C3–C4	1.467(13)	C23–C24	1.359(15)
Cr–N3	1.684(6)	C5–C6	1.455(14)	C24–C25	1.329(14)
Cr–C1	1.874(9)	C11–C12	1.368(14)	C25–C26	1.410(11)
Cr–C2	1.860(10)	C11–C16	1.396(11)	C31–C32	1.382(14)
Sn–C1	2.146(9)	C12–C13	1.378(15)	C31–C36	1.368(11)
Sn–C21	2.173(7)	C13–C14	1.364(14)	C32–C33	1.407(15)
Sn–C31	2.149(8)	C14–C15	1.352(13)	C33–C34	1.371(15)
O1–C1	1.138(10)	C15–C16	1.379(12)	C34–C35	1.352(15)
O2–C2	1.116(12)	C21–C22	1.376(12)	C35–C36	1.387(12)
O3–N3	1.187(8)				
Sn–Cr–N1	82.7(2)	N1–C4–C3	177.4(10)		
Sn–Cr–N2	86.7(2)	N2–C6–C5	179.1(10)		
Sn–Cr–N3	173.1(3)	Sn–C11–C12	122.8(6)		

(continued)

TABLE 6. *(continued)*

Sn–Cr–C1	85.2(3)	Sn–C11–C16	121.1(6)
Sn–Cr–C2	80.2(3)	C12–C11–C16	115.9(8)
N1–Cr–N2	84.8(3)	C11–C12–C13	122.6(9)
N1–Cr–N3	96.7(3)	C12–C13–C14	120.3(8)
N1–Cr–C1	166.8(3)	C13–C14–C15	118.5(8)
N1–Cr–C2	96.1(3)	C14–C15–C16	121.6(8)
N2–Cr–N3	100.1(3)	C11–C16–C15	120.9(8)
N2–Cr–C1	89.3(3)	Sn–C21–C22	123.8(6)
N2–Cr–C2	166.7(3)	Sn–C21–C26	119.5(5)
N3–Cr–C1	96.0(3)	C22–C21–C26	116.5(7)
N3–Cr–C2	93.0(4)	C21–C22–C23	122.4(8)
C1–Cr–C2	87.0(4)	C22–C23–C24	119.8(9)
Cr–Sn–C11	119.4(2)	C23–C24–C25	120.8(8)
Cr–Sn–C21	113.1(2)	C24–C25–C26	119.5(8)
Cr–Sn–C31	113.9(2)	C21–C26–C25	120.9(7)
C11–Sn–C21	103.3(3)	Sn–C31–C32	119.1(6)
C11–Sn–C31	104.5(3)	Sn–C31–C36	124.2(6)
C21–Sn–C31	100.5(3)	C32–C31–C36	116.7(8)
Cr–N1–C4	178.3(7)	C31–C32–C33	121.6(9)
Cr–N2–C6	173.7(7)	C32–C33–C34	119.9(9)
Cr–N3–O3	173.1(7)	C33–C34–C35	118.3(8)
Cr–C1–O1	176.5(8)	C34–C35–C36	121.8(8)
Cr–C2–O2	173.8(8)	C31–C36–C35	121.5(8)

TABLE 7. Infrared CO and NO stretching frequencies, data were taken in CH_3CN

Compound	νCO (cm^{-1})	νNO (cm^{-1})
$W(CO)_4(NO)(Sn(C_6H_5)_3)$	2099, 2015	1725
$Cr(CO)_4(NO)(Sn(C_6H_5)_3)$	2099, 2030	1751
$W(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$	1993, 1906	1624
$Cr(CO)_2(CH_3CN)_2(NO)(Sn(C_6H_5)_3)$	1986, 1912	1660

difference is only shortened by 0.26 Å. The difference in their configurations also reveals that the two C≡N distances in the W structure are seemingly different, 1.113 versus 1.159 Å, the one *trans* to NO being shorter; those in the Cr structure are the same.

Comparing with the reported Cr–Sn lengths, e.g., 2.654 Å in $Cr(CO)_5(C_5H_5N)(Sn(C_4H_9)_2)$ [10], 2.621 Å in $Cr(CO)_5(C_4H_8NS_2Sn(C_4H_9))$ [11], and 2.728, 2.719 and 2.695 Å in $N(C_2H_5)_4^+Cr(CO)_4(Sn(C_6H_5)_3)_3^-$ [12], and from the reported W–Sn lengths, e.g., 2.760, 2.783, 2.811 and 2.772 Å in $N(CH_3)_4^+((CH_3)_2CHO)W(CO)_3(Sn_4(C_6H_5)_{10})^-$ [13], 2.806 Å in $N(C_2H_5)_4^+W(C_2(C_6H_5)_2)_3(Sn(C_6H_5)_3)^-$ [14], 2.759 Å in $WCl(CO)_3(CH_3SC_2H_4SCH_3)(SnCl_2(CH_3))$ [15], 2.749 Å in $W(CO)_5(Sn(C_6H_3(CH_3)(N(CH_3)_2))_2)$ and 2.762 Å in $W(CO)_5(Sn(C_6H_3(CH_3)(P(C_6H_5)_2))_2)$ [16], the Cr–Sn length of 2.731 Å and the W–Sn length of 2.813 Å in this study are reasonable values taking into account the bulkiness of $Sn(C_6H_5)_3$. The Sn–C, phenyl C–C, C–O, N–O, and the M–C lengths are normal. The M–N–O angles are linear.

Acknowledgements

This work was financially supported by Academia Sinica and the National Science Council, Taiwan, to whom thanks are due.

References

1 (a) J. P. Collman, N. W. Hoffman and D. E. Morris, *J. Am. Chem. Soc., 91* (1969) 5659; (b) S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc., 92* (1971) 3068; (c) O. Crichton, M. Poliakoff, A. J. Rest and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, (1973) 1321.

2 C. M. Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole, Wadsworth, Belmont, CA, 1985, p. 317.

3 J. T. Lin, D. Fang and L. K. Liu, *Bull. Inst. Chem. Acad. Sin., 33* (1986) 63.

4 T. Hahn (ed.), *International Tables for X-ray Crystallography, Vol. A. Space-group Symmetry*, D. Reidel, Dordrecht, 1983.

5 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974. (Present distributor D. Reidel, Dordrecht.).

6 (a) R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey and R. Bau, *J. Am. Chem. Soc., 98*

(1976) 4491; (b) T. T. Malito, R. Shakir and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, (1980) 1253.

7 E. J. Gabe, F. L. Lee and Y. Le Page, The N.R.C. VAX Crystal Structure System, in G. M. Sheldrick, C. Krueger and R. Goddard (eds.), *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*, Clarendon, Oxford, 1985, pp. 167–174.

8 C. K. Johnson, *ORTEP, Report ORNL-3794*, Oak Ridge National Laboratory, TN, 1965.

9 (a) R. E. Marsh and F. H. Herbstein, *Acta Crystallogr., Sect. B, 39* (1983) 280; (b) *44* (1988) 77.

10 M. D. Brice and F. A. Cotton, *J. Am. Chem. Soc., 95* (1973) 4529.

11 A. Tzschach, K. Jurkschat, M. Scheer, J. Meunier-Piret and M. van Meerssche, *J. Organomet. Chem., 259* (1983) 165.

12 J. T. Lin, G. P. Hagen and J. E. Ellis, *Organometallics, 3* (1984) 1288.

13 G. L. Rochfort and J. E. Ellis, *J. Organomet. Chem., 250* (1983) 277.

14 J. M. Maher, J. R. Fox, B. M. Foxman and N. J. Cooper, *J. Am. Chem. Soc., 106* (1984) 2347.

15 M. Elder and D. Hall, *Inorg. Chem., 8* (1969) 694.

16 H.-P. Abicht, K. Jurkschat, A. Tzschach, K. Peters, E.-M. Peters and H. G. von Schnering, *J. Organomet. Chem., 326* (1987) 357.