Ligand Substitution of $[M(SnPh_3)(MeCN)_2(CO)_2(NO)]$ (M = Cr or W) and Crystal Structure of $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$†

Jiann T'suen Lin,* Chong Hsin Shan, Duencheng Fang, Ling-Kang Liu,* and Yu Hsiou
Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

$[M(SnPh_3)(MeCN)_2(CO)_2(NO)]$ [(**1**) M = Cr; (**2**) M = W] react with $P(OMe)_3$, PEt_3, and $[N(PPh_3)_2][S_2CNEt_2]$ to form the complexes $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$ (**3**), $[M(SnPh_3)\{P(OMe)_3\}_2(CO)_2(NO)]$ [(**4**) M = Cr; (**5**) M = W], $[M(SnPh_3)(PEt_3)_2(CO)_2(NO)]$ [(**6**) M = Cr; (**7**) M = W], and $[N(PPh_3)_2][M(SnPh_3)(S_2CNEt_2)(CO)_2(NO)]$ [(**8**) M = Cr; (**9**) M = W]. The structure of (**3**) has been determined by *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$ with a = 11.267(3), b = 13.025(3), c = 19.501(9) Å, β = 100.98(2)°, and Z = 4. Least-squares refinement based on 4 270 observed reflections led to a final R of 0.057.

Recently, we[1] reported the synthesis of the complexes $[M(SnPh_3)(MeCN)_2(CO)_2(NO)]$ [(**1**) M = Cr; (**2**) M = W]. Crystal structure determination for (**1**) and (**2**) has confirmed that the complexes adopt a configuration with *cis* CO groups and NO *trans* to $SnPh_3$.[2]

In this paper we describe our observations that the acetonitrile ligands in (**1**) and (**2**) are readily displaced by $P(OMe)_3$, PEt_3, and $S_2CNEt_2^-$. The complexes $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$ (**3**), $[M(SnPh_3)\{P(OMe)_3\}_2(CO)_2(NO)]$ [(**4**) M = Cr; (**5**) M = W], $[M(SnPh_3)(PEt_3)_2(CO)_2(NO)]$ [(**6**) M = Cr; (**7**) M = W], and $[N(PPh_3)_2][M(SnPh_3)(S_2CNEt_2)(CO)_2(NO)]$ [(**8**) M = Cr; (**9**) M = W] were isolated and characterized. We have also undertaken a single-crystal *X*-ray structure determination of complex (**3**).

Results and Discussion

Conversion of organometallic complexes to intermediates containing ligated solvents has been found useful in ligand substitution.[3a] We have applied this strategy successfully in ligand substitution of $[Cr(SnPh_3)(CO)_4(NO)]$ (**10**) and $[W(SnPh_3)(CO)_4(NO)]$ (**11**)[1] with $P(OMe)_3$, PEt_3, and $S_2CNEt_2^-$. Displacement of both ligated acetonitriles in (**1**) or (**2**) by these 'soft' ligands occurred readily under ambient conditions and led to complexes (**4**)—(**9**), whereas the same products [except (**9**)] could not be obtained from the thermal reaction of complex (**10**) or (**11**) with the above ligands.

The geometry in the six-co-ordinate complexes (**4**)—(**7**) can be assigned as *trans*-CO/CO, *trans*-P/P, *trans*-$NO/SnPh_3$, on the basis of the following physical data. Two CO stretching vibrations in the i.r., with relative intensities ranging from 1:22 to 1:25 (ratio of symmetric:asymmetric CO stretching vibrations), were observed indicating a deviation (could be up to 20°)‡ of two *trans* carbonyls from the ideal 180° disposition. Only one peak was observed in the ^{31}P n.m.r. spectrum for the ligated phosphines or phosphites, consistent with a *trans* orientation of the two phosphorus ligands. A rearrangement of the configuration upon replacement of both acetonitriles by phosphorus ligands and the distortion of two *trans* CO ligands could be steric in origin, *i.e.*, three bulky ligands $SnPh_3$ and two phosphorus ligands tend to avoid one another as much as possible. One speculative mechanism for the rearrangement would be the dissociation of MeCN from the monosubstituted product, $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$, forming a five-co-ordinate intermediate which then adds the second phosphorus ligand from the favoured position with regard to steric hindrance. Both complexes (**8**) and (**9**) exhibit two intense CO stretching frequencies with comparable intensities as well as two magnetically equivalent ethyl groups of the dithiocarbamate ligand, supporting the geometry: *cis*-CO/CO, *cis*-S/S, *trans*-$NO/SnPh_3$. Selective homodecoupling at the methyl group of the dithiocarbamate ligand simplifies the diastereotopic methylene protons to an AB quartet.

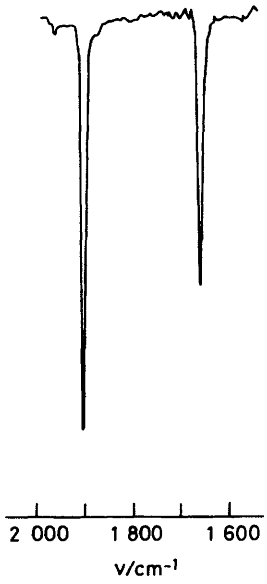

Figure 1. Infrared spectrum of $[Cr(SnPh_3)(PEt_3)_2(CO)_2(NO)]$ (**6**) in hexane from 1 600 to 2 000 cm^{-1}

Complex (**3**), the intermediate for complex (**4**), was isolated, if the reaction of (**1**) with $P(OMe)_3$ was performed at temperatures below −20 °C. The structure of (**3**) has been unambiguously assigned as *cis*-CO/CO, *cis*-$MeCN/P(OMe)_3$, *trans*-$NO/SnPh_3$ by a single-crystal *X*-ray structure determination. The structure of (**3**) together with the atom numbering scheme is shown in Figure 2. Selected bond distances and angles are given in Table 1. The co-ordination core about the chromium atom is close to an octahedron with slight distortion. The Cr–N(nitrosyl) distance (1.651 Å) is comparable with the corresponding distance in *trans*-$[\{Cr(\eta^5\text{-}C_5H_5)(NO)(SPh)\}_2]$ (1.66 Å),[4a] $[\{Cr(\eta^5\text{-}C_5H_5)$-

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† (Acetonitrile)dicarbonyl(nitrosyl)(trimethyl phosphite)(triphenylstannyl)chromium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ The i.r. spectrum of complex (**6**) is shown in Figure 1. The estimated angle $(2\theta)^{3b}$ between two CO ligands, C–Cr–C, is 156° for this complex.

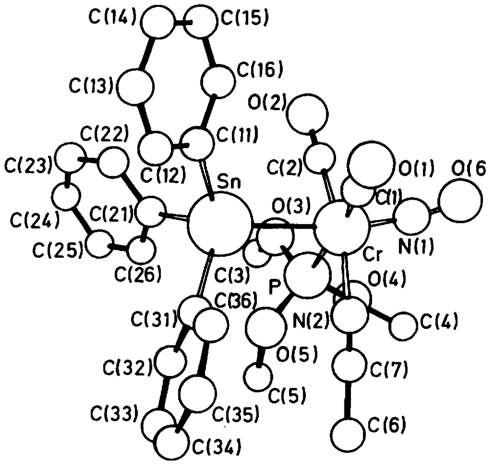

Figure 2. ORTEP drawing of the molecule $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$ (3) showing the atomic numbering sequence. The hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$

Cr–Sn	2.749(1)	Cr–P	2.323(2)
Cr–N(1)	1.651(6)	Cr–N(2)	2.063(6)
Cr–C(1)	1.845(7)	Cr–C(2)	1.799(8)
N(1)–O(6)	1.200(9)	C(1)–O(1)	1.153(9)
C(2)–O(2)	1.19(1)	N(2)–C(7)	1.090(9)
C(6)–C(7)	1.48(1)	Sn–C(11)	2.170(6)
Sn–C(21)	2.164(6)	Sn–C(31)	2.173(6)
Sn–Cr–P	88.67(6)	Sn–Cr–N(1)	171.0(2)
Sn–Cr–N(2)	88.1(1)	Sn–Cr–C(1)	80.5(2)
Sn–Cr–C(2)	81.3(2)	P–Cr–N(1)	96.9(2)
P–Cr–N(2)	84.6(1)	P–Cr–C(1)	167.8(2)
P–Cr–C(2)	90.5(2)	N(1)–Cr–N(2)	99.5(2)
N(1)–Cr–C(1)	94.7(3)	N(1)–Cr–C(2)	91.6(3)
N(2)–Cr–C(1)	89.4(2)	N(2)–Cr–C(2)	168.4(2)
C(1)–Cr–C(2)	93.5(3)	N(2)–C(7)–C(6)	179.3(8)
Cr–N(1)–O(6)	170.3(5)	Cr–N(2)–C(7)	174.1(5)
Cr–C(1)–O(1)	178.2(6)	Cr–C(2)–O(2)	178.0(6)

$(NO)(NMe_2)\}_2]$ (1.63 Å),[4b] $[Cr(\eta^5\text{-}C_5H_5)(NO)_2(NCO)]$ (1.716 Å),[4c] $[Cr(\eta^5\text{-}C_5H_5)(NO)_2Cl]$ (1.71 Å),[4d] $[\{Cr(\eta^5\text{-}C_5H_5)(NO)_2\}_2]$ (1.690 Å),[4e] and $[CrI(CO)_2(PMePh_2)_2(NO)]$ (1.705 Å).[4f] Consistent with the solid-state structure, the solution i.r. of (3) has two intense CO stretching frequencies. A five-bond coupling between methyl protons of co-ordinated acetonitrile and the phosphorus atom was observed in the ^1H n.m.r. spectrum with a coupling constant of 2.5 Hz. In comparison, Bohle and Roper[5] recently reported a five-bond coupling constant of 18 Hz between acetonitrile and a *trans* phosphorus atom.

Experimental

Instrumentation and general experimental techniques were as described earlier.[1] Complexes (1), (2), (10), and (11) were prepared as previously described.[1]

Synthesis of $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$ (3).—To a sample (400 mg, 0.70 mmol) of (1) was added cold $P(OMe)_3$ (15 cm^3) and the solution was stirred at −20 °C for 15 h. After removal of the solvent, the residue was recrystallized from Et_2O–hexane to afford orange powdery (3) (230 mg, 50%), m.p. 118 °C (decomp.) (Found: C, 45.45; H, 4.20; N, 4.20. $C_{25}H_{27}CrN_2O_6PSn$ requires C, 45.95; H, 4.15; N, 4.30%). $\nu_{max.}$(CO) 1 991s, 1 924s; $\nu_{max.}$(NO) 1 667s cm^{-1} (MeCN). ^1H N.m.r. (CD_3CN), δ 7.50 (15 H, m, Ph), 3.58 [9 H, d, J(PH) 10.8, OMe], 1.82 [3 H, d, J(PH) 2.5 Hz, MeCN].

Synthesis of $[Cr(SnPh_3)\{P(OMe)_3\}_2(CO)_2(NO)]$ (4).—To a sample (100 mg, 0.18 mmol) of (1) was added $P(OMe)_3$ (25 cm^3). The solution was stirred at room temperature for 24 h. Removal of the solvent and recrystallization from hexane provided yellow crystals of (4) (90 mg, 70%), m.p. 118 °C (Found: C, 42.25; H, 4.55; N, 2.05. $C_{26}H_{23}CrNO_9P_2Sn$ requires C, 42.4; H, 4.50; N, 1.90%). $\nu_{max.}$(CO) 1 980w, 1 943vs; $\nu_{max.}$(NO) 1 680s cm^{-1} (hexane). ^1H N.m.r. (CD_3CN), δ 7.46 (15 H, m, Ph), 3.43 [18 H, filled doublet, ^3J(PH) + ^5J(PH) 11.0 Hz, OMe]; $^{31}P\text{-}\{^1H\}$ n.m.r. (CD_3CN), 187.2 [singlet with satellites, $J(^{117,119}SnP)$ 309, 321 Hz, $P(OMe)_3$]. If the reaction was carried out at 70 °C, it was complete within 1 h. Complexes (5)—(7) were prepared similarly.

$[W(SnPh_3)\{P(OMe)_3\}_2(CO)_2(NO)]$ (5). Yellow crystals (54%), m.p. 95 °C (Found: C, 35.9; H, 3.90; N, 1.60. $C_{26}H_{23}NO_9P_2SnW$ requires C, 36.0; H, 3.85; N, 1.60%). $\nu_{max.}$(CO) 1 997w, 1 953vs; $\nu_{max.}$(NO) 1 649s cm^{-1} (hexane). ^1H N.m.r. (CD_3CN), δ 7.46 (15 H, m, Ph), 3.53 [18 H, t, ^3J(PH) + ^5J(PH) 11.5 Hz, OMe]; $^{31}P\text{-}\{^1H\}$ n.m.r. (CD_3CN), δ 138.4 [singlet with satellites, $J(^{183}WP)$ 430, $J(^{117,119}SnP)$ 196, 203 Hz].

$[Cr(SnPh_3)(PEt_3)_2(CO)_2(NO)]$ (6). Yellow crystals (71%), m.p. 118 °C (Found: C, 53.0; H, 6.35; N, 2.00. $C_{32}H_{35}CrNO_3P_2Sn$ requires C, 53.05; H, 6.25; N, 1.95%). $\nu_{max.}$(CO) 1 965w, 1 906vs; $\nu_{max.}$(NO) 1 665s cm^{-1} (hexane). ^1H N.m.r. (CD_3CN), δ 7.50 (15 H, m, Ph), 1.67 (12 H, m, CH_2), 1.00 (18 H, m, CH_3); $^{31}P\text{-}\{^1H\}$ n.m.r. (CD_3CN), 43.3 [singlet with satellites, $J(^{117,119}SnP)$ 252 Hz].

$[W(SnPh_3)(PEt_3)_2(CO)_2(NO)]$ (7). Yellow crystals (65%), m.p. 106 °C (Found: C, 44.8; H, 5.65; N, 1.75. $C_{32}H_{35}NO_3P_2SnW$ requires C, 44.9; H, 5.30; N, 1.65%). $\nu_{max.}$(CO) 1 981w, 1 919vs; $\nu_{max.}$(NO) 1 642s cm^{-1} (hexane). ^1H N.m.r. (CD_3CN), δ 7.50 (15 H, m, Ph), 1.74 (12 H, m, CH_2), 0.99 (18 H, m, CH_3); ^{31}P n.m.r. (CD_3CN), δ 139.0 [singlet with satellites, $J(^{183}WP)$ 436, $J(^{117,119}SnP)$ 202 Hz].

Synthesis of $[N(PPh_3)_2][Cr(SnPh_3)(S_2CNEt_2)(CO)_2(NO)]$ (8).—A MeCN solution containing (1) (150 mg, 0.26 mmol) and $[N(PPh_3)_2][S_2CNEt_2]$ (180 mg, 0.26 mmol) was stirred for 24 h at room temperature. Recrystallization from MeCN–EtOH gave orange powdery (8) (100 mg, 33%), m.p. 152 °C (decomp.) (Found: C, 62.05; H, 4.65; N, 3.75. $C_{61}H_{55}CrN_3O_3P_2S_2Sn$ requires C, 62.35; H, 4.70; N, 3.60%). $\nu_{max.}$(CO) 1 953s, 1 870s; $\nu_{max.}$(NO) 1 608s cm^{-1} (MeCN). ^1H N.m.r. (CD_3CN), δ 7.50 (45 H, m, Ph), 3.40 [4 H, m, CH_2; AB quartet with ^2J(HH) 13.6 for selective decoupling at 0.93 p.p.m.], 0.93 [6 H, t, ^3J(HH) 7.1 Hz, CH_3].

Synthesis of $[N(PPh_3)_2][W(SnPh_3)(S_2CNEt_2)(CO)_2(NO)]$ (9).—The same procedure for the synthesis of (8) was followed. Complex (9) was obtained as a yellow powder from (2) or (11) with yields of 56 and 70% respectively, m.p. 140 °C (decomp.) (Found: C, 56.05; H, 4.25; N, 3.25. $C_{61}H_{55}N_3O_3P_2S_2SnW$ requires C, 56.05; H, 4.25; N, 3.20%). $\nu_{max.}$(CO) 1 963s, 1 873s; $\nu_{max.}$(NO) 1 562m cm^{-1} (MeCN). ^1H N.m.r. (CD_3CN), δ 7.50 (45 H, m, Ph), 3.44 [4 H, m, CH_2; AB quartet with ^2J(HH) 14.5 for selective decoupling at δ 1.01], and 1.01 [6 H, t, ^3J(HH) 7.1 Hz, CH_3].

X-*Ray Analysis of Complex* (3).—Orange crystals of (3) were obtained by cooling of a near saturated MeCN solution to −4 °C for 24 h.

Table 2. Final fractional co-ordinates of non-hydrogen atoms for $[Cr(SnPh_3)(MeCN)\{P(OMe)_3\}(CO)_2(NO)]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	0.223 97(4)	0.193 17(3)	0.328 43(2)	C(11)	0.264 8(6)	0.035 0(5)	0.359 0(3)
Cr	0.418 37(9)	0.323 09(8)	0.363 12(5)	C(12)	0.228 3(7)	−0.047 5(6)	0.316 3(4)
P	0.283 82(17)	0.458 52(14)	0.361 50(10)	C(13)	0.249 1(7)	−0.147 5(6)	0.340 0(4)
O(1)	0.551 1(5)	0.128 6(4)	0.344 8(3)	C(14)	0.305 4(7)	−0.166 1(6)	0.407 5(4)
O(2)	0.391 0(5)	0.267 3(4)	0.507 4(3)	C(15)	0.343 2(7)	−0.087 9(6)	0.450 2(4)
O(3)	0.217 7(4)	0.459 0(3)	0.425 9(2)	C(16)	0.324 5(6)	0.013 3(6)	0.426 5(4)
O(4)	0.335 7(5)	0.573 3(4)	0.366 3(3)	C(21)	0.059 2(6)	0.210 9(5)	0.368 9(3)
O(5)	0.181 4(4)	0.459 5(4)	0.293 6(3)	C(22)	0.022 0(6)	0.134 3(5)	0.409 4(4)
O(6)	0.632 4(6)	0.428 3(5)	0.425 7(3)	C(23)	−0.086 9(7)	0.142 6(6)	0.433 6(4)
N(1)	0.542 6(6)	0.388 3(5)	0.394 0(3)	C(24)	−0.154 4(7)	0.225 8(6)	0.419 2(4)
N(2)	0.403 2(5)	0.354 5(4)	0.258 1(3)	C(25)	0.124 6(7)	0.304 8(6)	0.378 7(4)
C(1)	0.498 6(6)	0.203 0(6)	0.350 8(4)	C(26)	−0.015 3(6)	0.295 6(5)	0.355 2(3)
C(2)	0.399 6(7)	0.289 0(6)	0.449 8(4)	C(31)	0.167 8(5)	0.190 4(5)	0.215 5(3)
C(3)	0.133 8(7)	0.538 5(6)	0.439 7(4)	C(32)	0.078 0(6)	0.254 1(5)	0.182 7(4)
C(4)	0.430 1(9)	0.605 1(7)	0.332 3(5)	C(33)	0.048 5(6)	0.259 2(6)	0.109 2(4)
C(5)	0.117 6(9)	0.544 7(8)	0.258 1(5)	C(34)	0.111 3(6)	0.199 9(6)	0.071 3(4)
C(6)	0.358 8(8)	0.393 9(7)	0.127 1(5)	C(35)	0.199 2(6)	0.136 4(5)	0.101 6(4)
C(7)	0.384 9(7)	0.371 5(6)	0.202 4(4)	C(36)	0.230 5(6)	0.130 0(5)	0.175 0(4)

Crystal data. $C_{25}H_{27}CrN_2O_6PSn$, $M = 653.2$, monoclinic, $a = 11.267(3)$, $b = 13.025(3)$, $c = 19.501(9)$ Å, $\beta = 100.98(2)°$, $U = 2\,809$ Å^3, $\lambda = 0.709\,30$ Å, space group $P2_1/c$, $Z = 4$, $D_c = 1.544$ g cm^{-3}, $F(000) = 1\,312$, $\mu(\text{Mo-}K_\alpha) = 13.64$ cm^{-1}.

Data collection and processing. CAD-4 diffractometer, ω scan width = (1.4 + 0.70 tanθ)°, ω scan speed 1.2—6.7° min^{-1}, graphite-monochromated Mo-K_α radiation; 4 931 reflections measured ($0 \leqslant 2\theta \leqslant 50°$, $\pm h$, $+k$, $+l$), 4 270 being considered observed [$I \geqslant 2.5\sigma(I)$].

Structure analysis and refinement. This was carried out using programs from the National Research Council of Canada PDP-11 package.[6] The Sn atom was determined by Patterson synthesis; all other atoms were located by subsequent difference Fourier maps and cycles of least-squares refinement. The Sn, Cr, and P atoms were refined anisotropically, and all other non-hydrogen atoms isotropically. Hydrogen atoms were included in the final refinement. $R = 0.057$, $R' = 0.058$, $S = 8.2339$ based on F, with $w = 1/\sigma^2(F_o)$. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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