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Schiff Base Derivatives of Chromium Carbonyl

S. C. TRIPATHI*, S. C. SRIVASTAVA, A. K. SHRIMAL and O. P. SINGH
Department of Chemistry, University of Gorakhpur, Gorakhpur, India

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Abstract

N,N'-Ethylenebis(benzalideneimine) (SB^1), N,N'-ethylenebis(*p*-anisylideneimine) (SB^2), N,N'-ethylenebis(methylphenylketimine) (SB^3) and N,N'-ethylenebis(diphenylketimine) (SB^4) reacted with chromium hexacarbonyl to give *cis*-disubstituted derivatives. Schiff base (SB) bridged dinuclear derivatives, $(Ph_3E)(CO)_4Cr$-μ-(SB)-$Cr(CO)_4(Ph_3E)$ were obtained by refluxing $(Ph_3E)Cr(CO)_5$ (E = P and As) and SB in toluene. Bromine and iodine oxidation of *cis*-(SB)$Cr(CO)_4$ gave a mixture of CO free products, (SB)CrX_2 (X = Br and I) and CrX_2. Nitrosylation of *cis*-(SB)$Cr(CO)_4$ using NO-swept benzene was also investigated.

Introduction

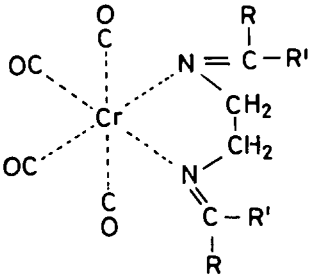
Although there has been considerable study of the ligand behaviour of a quadridentate Schiff base [1, 2], N,N'-ethylenebis(salicylideneimine) with $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co_2(CO)_8$, $Ni(CO)_4$, $Ru_3(CO)_{12}$, $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$ in which non-carbonyl derivatives have been recovered in most cases, it is surprising that bidentate Schiff bases containing only two azomethine groups unaided by phenolic OH or N or S of the aromatic ring are almost unfamiliar. The first true carbonyl complexes of group VI metals were isolated only in 1972, when the reactions of 2-pyridine-carboxaldehydeimines, RN = CHC_5H_4N (N = Me, iso-Pr, C_6H_{11}, Ph or H) were investigated [3] under UV irradiation conditions. Since then only a few mono- [4–8] and *cis*-disubstitution [7–10] products have been reported.

We have used four Schiff bases, namely N,N'-ethylenebis(benzalideneimine) (SB^1), N,N'-ethylenebis(*p*-anisylideneimine) (SB^2), N,N'-ethylenebis(methylphenylketimine) (SB^3) and N,N'-ethylenebis(diphenylketimine) (SB^4) as ligands in the CO displacement reactions of $Cr(CO)_6$, (L–L)$Cr(CO)_4$ (L–L = *o*-phen or bipy) and $(Ph_3E)Cr(CO)_5$ (E = P and As). Bromine or iodine oxidation and nitrosylation of *cis*-(SB)$Cr(CO)_4$ was also attempted.

Results and Discussion

SB^1–SB^4 reacted with chromium hexacarbonyl in boiling toluene under argon during 6–8 h to give *cis*-(SB^1–SB^4)$Cr(CO)_4$. Schiff base bridged dinuclear $(CO)_5Cr$-μ-(SB)-$Cr(CO)_5$ and $(CO)_4Cr$-μ-$(SB)_2$-$Cr(CO)_4$ derivatives could not be recovered in any case, in contrast to other bidentate ligands [11, 12] in which two different donor sites are bonded through two different $M(CO)_n$ moieties. Repeated attempts to achieve more substitution by prolonged refluxing or by heating the reactants in evacuated sealed pyrex tubes up to 200 °C were unsuccessful.

All the (SB)$Cr(CO)_4$ derivatives are yellow to orange crystalline solids which dissolve in both polar and nonpolar organic solvents, except light petroleum (all fractions). These derivatives exhibited four CO stretching bands (Table I) due to $2a_1 + b_1 + b_2$ modes of C_{2v} symmetry in agreement with their *cis*-configurations (Structure I). The medium strong band at 1995–2000 cm^{-1} is assigned to $a_1^{(1)}$ mode, which mainly involves *trans* carbonyl groups. Bands in the ranges 1880–1890, 1860–1870 and 1805–1830 cm^{-1} may be attributed to modes b_1, $a_1^{(2)}$ and b_2, respectively. The Cotton and Kraihanzel [13] force constants k_1 and k_2 of CO groups *trans* and *cis* to the substituent nitrogen atoms, respectively and the stretch-stretch interaction constant, k_i, have also been deduced. The values of k_1, k_2 and k_i for these derivatives (Table I) are in the ranges 13.51–13.90, 15.04–15.16 and 0.35–0.38 mdynes/Å, respectively. These



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(where R = H, R = C_6H_5 or $C_6H_5(OCH_3)$; R = CH_3, R' = C_6H_5; R = C_6H_5, R' = C_6H_5)

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*Author to whom correspondence should be addressed.

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TABLE I. CO Stretching Frequencies and CO Force Constants of *cis*-(SB)Cr(CO)$_4$ Complexes.

Complex	ν_{CO} (cm^{-1})	Force constants (mdynes/Å)		
		k_1	k_2	k_i
(SB^1)Cr(CO)$_4$	1995m (a$_1^1$), 1890sh (b$_1$) 1860s (a$_1^2$), 1805s (b$_2$)	13.51	15.13	0.35
(SB^2)Cr(CO)$_4$	2000m (a$_1^1$), 1885s (b$_1$) 1870s (a$_1^2$), 1818s (b$_2$)	13.73	15.11	0.38
(SB^3)Cr(CO)$_4$	2000m (a$_1^1$), 1890sh (b$_1$) 1867s (a$_1^2$), 1817s (b$_2$)	13.70	15.16	0.36
(SB^4)Cr(CO)$_4$	2000m (a$_1^1$), 1880s (b$_1$) 1870s (a$_1^2$), 1830s (b$_2$)	13.90	15.04	0.38

TABLE II. CO Stretching Frequencies for SB Bridged (Ph$_3$E)(CO)$_4$Cr-μ-(SB)-Cr(CO)$_4$(Ph$_3$E) Complexes.

Complex	ν_{CO} (cm^{-1})
(Ph$_3$P)(CO)$_4$Cr-μ-(SB^2)-Cr(CO)$_4$(Ph$_3$P)	2005w, 1962m, 1888s
(Ph$_3$P)(CO)$_4$Cr-μ-(SB^4)-Cr(CO)$_4$(Ph$_3$P)	2010w, 1940m, 1880s
(Ph$_3$As)(CO)$_4$Cr-μ-(SB^2)-Cr(CO)$_4$(Ph$_3$As)	2015m, 1965m, 1895s
(Ph$_3$As)(CO)$_4$Cr-μ-(SB^4)-Cr(CO)$_4$(Ph$_3$As)	2010w, 1960s, 1882s

values are in close resemblance to the values of force constants deduced for other N donor containing *cis*-disubstituted group VI metal carbonyls, confirming the validity of the vibrational mode assignments. Since the force constants have been calculated from frequencies of spectra in KBr discs they can be considered as lower limits and might well be 0.10–0.20 units higher if obtained from solution data.

A small shift of ~10–20 cm^{-1} in $\nu_{C=N}$ (SB^1: 1640, Cr(CO)$_4$SB^1: 1620; SB^2: 1610, Cr(CO)$_4$SB^2: 1600; SB^4: 1660, Cr(CO)$_4$SB^4: 1650 cm^{-1}) of coordinated Schiff bases in these derivatives indicates only N lone pair donation and almost no involvement of a CN double bond.

Mixed ligand (L–L)Cr(CO)$_3$L (L–L = *o*-phen or bipy; L = N, P, As and Sb donors) derivatives are easily obtained by refluxing (L–L)Cr(CO)$_4$ and L in hydrocarbon solvents or neat in case L is liquid. Organic phosphites are capable of displacing more CO to yield (L–L)Cr(CO)$_2$L$_2$. On performing similar reactions Schiff bases could not displace CO from (L–L)Cr(CO)$_4$ when refluxed in THF or hydrocarbon solvents for 2–20 h, or even in evacuated sealed pyrex tubes upto 200 °C. In spite of the easy chances for chelation such inert behaviour of these ligands may be attributed to the decreased basicity of azomethine nitrogen compared to other mono and polydentate nitrogen donors. The decreased donor behaviour of Schiff bases was further exhibited when *o*-phen or 2,2′-bipy displaced them from *cis*-(SB)Cr(CO)$_4$, even at room temperature. Another interesting type of reaction was that between SB and (Ph$_3$E)Cr(CO)$_5$ in which SB displaced CO leaving Ph$_3$E (E = P and As) intact in the resulting (Ph$_3$E)(CO)$_4$Cr-μ-(SB)-Cr(CO)$_4$(Ph$_3$E) derivatives. The IR spectra of all the derivatives exhibited two very strong bands, one between 1940–1965 cm^{-1} and the other between 1880–1895 cm^{-1}, in addition to a weak-to-medium intensity band at ~2010 cm^{-1} (Table II).

These spectral patterns resemble closely the patterns of the reported [11] diphenylstibinomethane bridged [Cr(CO)$_4$]$_2$(Ph$_2$SbCH$_2$SbPh$_2$)$_2$ derivative (ν_{CO}: 2008, 1919, 1898 cm^{-1}). The lowest frequency band in the spectra of these derivatives is ~60 cm^{-1} in the higher region than *cis*-(SB)Cr(CO)$_4$ derivatives, which may be attributed to the presence of better acceptor triphenylphosphine or triphenylarsine. The $\nu_{C=N}$ stretching bands of coordinated SB are nearly unshifted in these molecules. The nature and number of CH$_2$ bands in these derivatives agree well with the *trans*-CH$_2$ configurations similar to disubstituted ethanes [14]. Cryoscopic determination of molecular weights of these derivatives (Table III) further established their dinuclear formulation. In a different type of reaction Ph$_3$E displaced SB easily from *cis*-(SB)Cr(CO)$_4$ to give *cis*-(Ph$_3$E)$_2$Cr(CO)$_4$.

Halogen Oxidation of cis-(SB)Cr(CO)$_4$

Bromine or iodine reacted briskly with *cis*-(SB)Cr(CO)$_4$ when a benzene solution of appropriate

TABLE III. Preparative Conditions, Colour and Analyses of Complexes.

Complex	Reaction time (h)	Colour	Yield (%)	Mol. cond. (ohm^{-1} cm^2)	Mol. wt.	Mag. mon. (B.M.)	Found (Calcd) %			
							C	H	N	Hal.
$(SB^2)Cr(CO)_4$	8	Orange yellow	25.0				58.1 (57.4)	4.6 (4.4)	6.2 (6.1)	
$(SB^3)Cr(CO)_4$	7	Yellow	39.5				61.5 (61.7)	4.9 (4.7)	6.6 (6.5)	
$(SB^4)Cr(CO)_4$	9	Orange	43.0				69.0 (69.6)	4.3 (4.4)	4.9 (5.1)	
$(Ph_3P)(CO)_4Cr\text{-}\mu\text{-}(SB^2)\text{-}Cr(CO)_4(Ph_3P)$	7	Yellow	54.0		1105 (1148)		63.9 (64.8)	4.2 (4.3)	2.4 (2.4)	
$(Ph_3P)(CO)_4Cr\text{-}\mu\text{-}(SB^4)\text{-}Cr(CO)_4(Ph_3P)$	8	Yellow-brown	57.0		1180 (1240)		68.8 (69.6)	4.1 (4.3)	2.3 (2.2)	
$(Ph_3As)(CO)_4Cr\text{-}\mu\text{-}(SB^2)\text{-}Cr(CO)_4(Ph_3As)$	8	Yellow green	52.0		1188 (1236)		59.6 (60.2)	3.9 (4.1)	2.1 (2.3)	
$(Ph_3As)(CO)_4Cr\text{-}\mu\text{-}(SB^4)\text{-}Cr(CO)_4(Ph_3As)$	6	Olive-green	42.0		1290 (1328)		64.2 (65.1)	3.9 (4.1)	2.0 (2.1)	
$Cr(SB^2)I_2$		Yellow	60.2	0.4[a]		4.8	34.9 (35.4)	3.5 (3.3)	4.6 (4.1)	43.0 (43.2)
$Cr(SB^3)I_2$		Yellow	57.3	0.6[a]		4.7	37.3 (37.9)	3.4 (3.5)	5.0 (4.9)	45.2 (44.5)
$Cr(SB^4)I_2$		Yellow	63.2	0.5[a]		4.8	46.9 (48.4)	3.4 (3.4)	3.9 (4.0)	36.8 (36.6)
$Cr(SB^1)Br_2$		Brown	53.2	0.7[a]		4.8	43.1 (43.8)	3.3 (3.6)	6.2 (6.3)	34.9 (35.7)
$Cr(SB^2)Br_2$		Brown	59.6	0.5[a]		4.9	41.9 (42.5)	3.7 (3.9)	5.4 (5.5)	31.6 (31.5)
$Cr(SB^3)Br_2$		Brown	42.0	0.6[a]		5.0	44.6 (45.4)	4.1 (4.2)	5.8 (5.9)	33.4 (33.6)
$Cr(SB^4)Br_2$		Brown	62.7	0.5[a]		5.0	55.6 (56.0)	4.1 (4.0)	4.5 (4.7)	26.4 (26.7)
$(NO)_2(SB^2)Cr(NO_2)_2$		Yellow	47.5	0.5[b]			42.6 (43.2)	3.8 (4.0)	16.7 (16.8)	
$(NO)_2(SB^3)Cr(NO_2)_2$		Yellow	48.2	0.5[b]			42.8 (43.2)	3.9 (4.0)	16.7 (16.8)	
$(NO)_2(SB^4)Cr(NO_2)_2$		Yellow	53.7	0.8[b]			55.9 (56.7)	3.9 (4.0)	14.3 (14.1)	

[a] In dichloromethane. [b] In acetone.

halogen was added dropwise to a well-stirred benzene solution of the carbonyl under argon. Precipitation occurred instantaneously leaving an almost colourless supernatant liquid in all cases. Extraction of the precipitate with dichloromethane left undissolved red (in case of iodination) or white (bromination) CrX_2 (X = Br or I). Evaporation of dichloromethane from the extract yielded $(SB)CrX_2$ as yellow solids, which gave non-conducting solutions (Λ_m = 0.4 to 0.7 ohm^{-1} cm^2 in dichloromethane) and which exhibited magnetic moments of 4.7–5.0 B.M. Their IR spectra showed them to be non-carbonyl complexes and only SB bands appeared in all cases. They may be treated as adducts similar to $CrX_2(py)_2$ [15] (py = 3-chloro-, 3-bromo-, 3-iodo-, 2,5-dichloropyridine; X = Cl, Br, I).

Nitrosylation of cis-(SB)Cr(CO)$_4$

Nitric oxide reacted instantaneously with *cis*-$(SB)Cr(CO)_4$ by displacing CO at room temperature to give non-carbonyl derivatives, $(NO)_2(SB)Cr(NO_2)_2$, which contained both nitrosyl and nitro groups. They were insoluble in C_6H_6, Et_2O and CCl_4 but dissolved in Me_2CO, CH_2Cl_2 and THF. All the derivatives exhibited non-conducting behaviour in acetone and were diamagnetic. Their IR spectra, in addition to the SB band, exhibited only two N–O bands in the ranges 1750–1785 cm^{-1}, together with a weak satellite at 1320 cm^{-1} in all the derivatives, indicating unequivocally the presence of a nitro group.

Although derivatives containing NO^+, NO^-, bridging NO and $N_2O_2^{2-}$ are already known to form by direct action of NO on metal carbonyl species, these chromium derivatives are probably the first examples of other than the known ones. A similar result has been previously reported for a nickel derivative by Feltham [16], who studied the reaction of $Ni(CO)_2(PPh_3)_2$ with NO in the presence of NO_2 to give $Ni(NO)(PPh_3)_2NO_2$. In the present study the formation of such derivatives is not obvious. It is possible that originally only nitrosyl products are formed, which ultimately change into nitro products during isolation as a result of aerial oxidation.

Experimental

All the experiments were performed in argon atmosphere or *in vacuo*. Conductivity measurements were made on a Toshniwal conductivity bridge (Type CL 01/02A). Magnetic measurements were done with a polytronic electromagnet (type EM-100, SR No. 113), using a Keroy magnetic balance with sensitivity 10^{-5} g. Infrared spectra were measured on a Beckman Spectrophotometer (AccuLab 9) in KBr discs. Halogens were estimated gravimetrically, by precipitating their corresponding silver salts. Molecular weight determinations were made by a cryoscopic method. Schiff bases were prepared by condensing the appropriate aldehydes or ketones with ethylenediamine in methanol and were recrystallized in benzene. Nitric oxide was prepared by the interaction of sodium nitrite and acidified ferrous sulphate solution and the gas was purified by passing it through a concentrated solution (50%) of sodium hydroxide.

Preparation of N,N'-ethylenebis(benzalideneimine)-tetracarbonylchromium(0)

Hexacarbonylchromium(0) (0.2 g) and N,N'-ethylenebis(benzalideneimine) (0.21 g) were refluxed in toluene (15 ml) for 6 h under argon, during which the colour of the reaction mixture turned orange. After cooling the reaction mixture, the solvent was removed *in vacuo*. The residue was washed with light petroleum (40–60°) to remove unreacted reactants. The red solid was crystallized in benzene and was shown as N,N'-ethylenebis(benzalideneimine)tetracarbonylchromium(0) (0.12 g, 35%) *Anal.* Found: C, 59.8; H, 4.1; N, 6.9. $C_{20}H_{16}N_2O_4Cr$ calcd: C, 60.0; H, 4.0; N, 7.0%). IR: ν_{CO}: 1995 m, 1890 sh, 1860 s and 1805 s cm^{-1}.

Preparation of Bis(triphenylphosphine)-μ-N,N'-ethylenebis(benzalideneimine)octacarbonyldichromium(0)

(Triphenylphosphine) pentacarbonylchromium (0) (0.20 g) and N,N'-ethylenebis(benzalidineimine) (0.05 g) were refluxed in toluene (15 ml) for 7 h under argon. The colour of the reaction mixture turned yellowish-green. After cooling the reaction mixture to room temperature, the solvent was removed *in vacuo*. The unreacted (triphenylphosphine)pentacarbonylchromium(0) and SB were removed by washing the residue with light petroleum (40–60°) several times, and the yellow-green residue was crystallized in benzene. It was shown as bis(triphenylphosphine)-μ-N,N'-ethylenebis(benzalideneimine)octacarbonyldichromium(0) (0.12 g, 48%). *Anal.* Found: C, 68.2, H, 4.1, N, 2.5. $C_{60}H_{46}O_8N_2P_2Cr_2$ calcd: C, 68.7, H, 4.2, N, 2.5%. Mol. wt. (Found: 1048; calcd: 1088). IR: ν_{CO}: 2000 w, 1940 m and 1886 s cm^{-1}.

Preparation of Diiodo(N,N'-ethylenebis(benzalideneimine))chromium(II)

A solution of iodine (0.13 g) in benzene (50 ml) was added dropwise to a solution of N,N'-ethylenebis(benzalideneimine)tetracarbonylchromium(0) (0.2 g) in benzene (20 ml) at room temperature (~25 °C). The reaction mixture was stirred magnetically and after 20 min a yellow precipitate appeared in the reaction flask. Evolution of CO took place in form of brisk effervescence. The precipitate was filtered and washed several times with benzene to remove unreacted reactants if any. On washing the precipitate with dichloromethane, a red brown residue remained undissolved which was characterised as CrI_2. *Anal.*

Found: I, 82.7; calcd: I, 83.0% (μ_{eff} = 5.0 B.M.). On evaporating the dichloromethane washing a yellow product was obtained which was characterized as diiodo(N,N′-ethylenebis(benzalideneimine))chromium(II). *Anal.* Found: C, 34.9; H, 2.9; N, 5.3; I, 47.9. $C_{16}H_{16}N_2I_2Cr$ calcd: C, 35.4; H, 3.0, N, 5.2; I, 46.9%. Yield. 0.15 g, 53.6%. μ_{eff} = 4.9 B.M.

Preparation of Dinitro(N,N′-ethylenebis(benzalideneimine))dinitrosylchromium(0)

NO-swept benzene was added dropwise to a benzene solution of N,N′-ethylenebis(benzalideneimine)tetracarbonylchromium(0) (0.20 g) under argon at room temperature with constant stirring. After 1 h a yellow precipitate settled at the bottom of the reaction vessel. The precipitate was filtered and washed several times with benzene to remove any traces of parent carbonyl left unreacted; it was dried *in vacuo* and was shown as dinitro(N,N′-ethylenebis(benzalideneimine))dinitrosylchromium(0). *Anal.* Found: C, 42.9; H, 2.6; N, 21.5. $C_{16}H_{16}O_6N_6Cr$ calcd: C, 43.2; H, 2.6; N, 21.6%. Yield. 0.10 g, 47.6%. Λ_m = 0.8 ohm^{-1} cm^2 in acetone.

Other derivatives prepared are given in Table III.

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