

Synthesis of Alkylidyne Complexes of $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CC}_6\text{H}_4\text{Me}$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$). Crystal Structure of $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CC}_6\text{H}_4\text{Me}$

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The reaction of $(\text{CO})_2\text{M}=\text{C}(\text{OMe})\text{Tol}$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$ and $\text{Tol}=\textit{p}\text{-C}_6\text{H}_4\text{Me}$) and BBr_3 followed by treatment with tetramethylethylenediamine (TMEDA) yields a mixture of two diastereomers, *trans, cis*- $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CTol}$ [$\text{M}=\text{Cr}$ (1a), Mo (2a), W (3a)] and *cis, trans*- $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CTol}$ [$\text{M}=\text{Cr}$ (1b), Mo (2b), W (3b)], respectively. These compounds have been isolated as crystalline solids and characterized by spectroscopic (infrared, mass, ^1H and ^{13}C -NMR) data. The *trans, cis*- $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$ (1a), has been examined *via* a single crystal X-ray diffraction study: $\text{BrCrO}_2\text{N}_2\text{C}_{15}\text{H}_{23}$, $\text{Mr}=407.27$, triclinic, $P\bar{1}$, $a=12.792(2)$, $b=13.400(5)$, $c=11.645(4)$ Å, $\alpha=101.26(2)^\circ$, $\beta=103.04(2)^\circ$, $\gamma=91.88(2)^\circ$, $V=1907(1)$ Å³, $Z=2$, $\rho(\text{calcd})=1.418$ g cm⁻³, $\lambda(\text{MoK}\alpha)=0.71069$ Å, $\mu=26.25$ cm⁻¹, $F(000)=831.97$, $T=295$ K, $R=0.0977$ for 1332 significant reflections [$F_o > 5\sigma(F_o)$]. There are two essentially equivalent molecules in the crystallographic asymmetric unit. Each molecule is octahedral with the bromide ligand *trans* to the alkylidyne carbon, the two *cis*-carbonyl ligands, and the bidentate TMEDA ligand.

Introduction

There have been considerable interests in the chemistry of transition-metal alkylidyne complexes having a metal-carbon triple bond ($\text{M}\equiv\text{C}$), since the first alkylidyne complexes were reported by Fischer and co-workers in 1973¹. Metal alkylidyne complexes have been shown to be useful precursors for synthetic use², and active catalysts for alkyne metathesis³ and polymerization⁴. Bonding nature of the complexes has also been investigated⁵. Stone has made extensive use of the alkylidyne complexes as reagents for the synthesis of polynuclear metal compounds to investigate the reactivity of the bridging alkylidyne ligands present in the various products⁶. We have also utilized the Fischer's group 6 metal alkylidyne complexes to prepare group 6-triosmium mixed-metal cluster compounds⁷. For further exploration of our work, nitrogen donor-substituted alkylidyne complexes, $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CTol}$ [$\text{M}=\text{Cr}$ (1), Mo (2), and W (3), $\text{Tol}=\textit{p}\text{-C}_6\text{H}_4\text{Me}$, $\text{tmeda}=\text{tetramethylethylenediamine}$] have been prepared. Mayr *et al.* recently reported synthesis of the analogous TMEDA-substituted alkylidyne complexes, $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CPh}$ ⁸. They found that the complexes exist as a single isomer and assumed that the structure is that reported for a bromo tungsten alkylidyne complex, *trans, cis*- $\text{Br}(\text{CO})_2(\text{py})_2\text{W}\equiv\text{CPh}$, containing two donor ligands (pyridine) and two acceptor ligands (CO) with the bromo ligand *trans* to the alkylidyne and the carbonyl ligands *cis* to each other⁹. We, however, observed that complexes 1, 2 and 3 exist as two isomers in solution. Herein we report details of synthesis and characterization of compounds 1, 2 and 3 together with the X-ray structural analysis of one of the isomers, *trans, cis*- $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$ (1a).

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen with use of standard Sch-

lenk techniques. Solvents were dried prior to use. Alkylidyne complexes, $(\text{CO})_2\text{M}=\text{C}(\text{OMe})\text{Tol}$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$), were prepared as described in the literature^{9a,10}. Infrared spectra were obtained with a Bomem MB-100 FT-IR spectrophotometer. Both ^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded by the staff of the Analytical Laboratory at the Korean Advanced Institute Science and Technology using a Hewlett-Packard 5985B mass spectrometer. All m/z values are referenced Cr^{52} , Br^{79} , Mo^{96} and W^{184} . Micro-analytical data were provided by the Analytical Laboratory of the Agency for Defense Development.

Preparation of $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$. A solution of $(\text{CO})_2\text{Cr}=\text{C}(\text{OMe})\text{Tol}$ (2.00 g, 6.13 mmol) in petroleum ether (250 mL) at -20°C was treated with BBr_3 (8 mL of 1.0 M solution in hexane, 8 mmol), whereby a yellow precipitate, $\text{Br}(\text{CO})_2\text{Cr}\equiv\text{CTol}$, formed immediately. The reaction mixture was stirred at -20°C for 1.5 h. After the supernatant was decanted off, the yellow precipitate was washed with petroleum ether (3×10 mL) at -20°C and dried *in vacuo*. This material was dissolved in dichloromethane (200 mL) at -30°C and then TMEDA (4.6 mL, 30 mmol) was added. The solution was warmed to room temperature, during which time the color changed to red and stirred for 3 h. The solvent was removed to give a red solid. The residue was washed with petroleum ether and recrystallized with a mixture of chloroform and diethylether to afford a deep red crystalline solid (1, 1.90 g, 4.65 mmol, 76%, $1\text{a} : 1\text{b} = 1 : 1.1$): ^1H -NMR (CDCl_3 , 25°C) δ 7.35-7.03 (two set's of AB patterns, 8H, 1a, 1b, C_6H_4), 3.06 (s, 6H, 1a, $\text{CH}_3\text{-tmeda}$), 3.03 (s, 6H, 1b, $\text{CH}_3\text{-tmeda}$), 2.80 (s, 6H, 1a, $\text{CH}_3\text{-tmeda}$), 2.69 (s, 6H, 1b, $\text{CH}_3\text{-tmeda}$), 2.63 (s, 4H, 1a, $\text{CH}_2\text{-tmeda}$), 2.60 (s, 4H, 1b, $\text{CH}_2\text{-tmeda}$), 2.32 (s, 3H, 1b, $\text{CH}_3\text{-Tol}$), 2.31 (s, 3H, 1a, $\text{CH}_3\text{-Tol}$); ^{13}C -NMR (CDCl_3 , 25°C) δ 301.1 (1a, CTol), 298.2 (1b, CTol), 230.9 (1b, CO), 230.4 (1a, CO), 144.5 (1a, 1b, $\text{C}_{\text{ipso-Tol}}$), 139.0 (1a, $\text{C}_\beta\text{-Tol}$), 138.8 (1b, $\text{C}_\beta\text{-Tol}$), 129.1, 128.9, 128.7, 128.6 (1a, 1b, C_α & $\text{C}_\omega\text{-Tol}$), 59.7 (1a, $\text{CH}_2\text{-tmeda}$),

59.5 (1b, $\text{CH}_2\text{-tmeda}$), 57.0 (1a, $\text{CH}_3\text{-tmeda}$), 56.8 (1b, $\text{CH}_2\text{-tmeda}$), 52.8 (1a, $\text{CH}_3\text{-tmeda}$), 51.3 (1b, $\text{CH}_3\text{-tmeda}$), 21.4 (1a, $\text{CH}_3\text{-Tol}$), 21.3 (1b, $\text{CH}_3\text{-Tol}$); IR (KBr pellet) $\nu(\text{CO})$ 1993(s), 1921(s), 1903(s) cm^{-1} ; MS (70 eV) m/z 220. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2\text{BrCr}$: C, 47.2; H, 5.69; N, 6.88. Found: C, 48.6; H, 5.54; N, 6.85.

Preparation of $\text{Br}(\text{CO})_2(\text{tmeda})\text{Mo}=\text{CTol}$. A solution of $(\text{CO})_5\text{Mo}=\text{C}(\text{OMe})\text{Tol}$ (0.50 g, 1.35 mmol) in petroleum ether (100 mL) was treated with BBr_3 (1.8 mL of 1.0 M solution in hexane, 1.75 mmol) at -30°C to generate $\text{Br}(\text{CO})_4\text{Mo}=\text{CTol}$. The reaction mixture was stirred at -30°C for 1 h, the supernatant was decanted off, and the yellow residue was washed with petroleum ether (100 mL) at -20°C . After evaporation of solvent *in vacuo*, it was redissolved in dichloromethane (100 mL) at -20°C and TMEDA (1.0 mL, 6.5 mmol) was added. The temperature was slowly raised to 0°C in an ice bath and the reaction mixture was stirred for 2 h. After evaporation of the solvent, the residue was washed with petroleum ether (2 \times 20 mL) at 0°C and recrystallized with a mixture of chloroform and diethylether to give a golden yellow crystalline solid (2, 0.34 g, 0.75 mmol, 56%, $2\mathbf{a} : 2\mathbf{b} = 1 : 6.6$): $^1\text{H-NMR}$ (CDCl_3 , 0°C) δ 7.28-6.90 (m, 8H, $2\mathbf{a}$, $2\mathbf{b}$, C_6H_4), 3.09 (s, 6H, $2\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 3.06 (s, 6H, $2\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 2.91 (s, 6H, $2\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 2.83 (s, br, 10H, $2\mathbf{b}$, CH_3 , $\text{CH}_2\text{-tmeda}$), 2.80 (s, 4H, $2\mathbf{a}$, $\text{CH}_2\text{-tmeda}$), 2.32 (s, 3H, $2\mathbf{b}$, $\text{CH}_3\text{-Tol}$), 2.31 (s, 3H, $2\mathbf{a}$, $\text{CH}_3\text{-Tol}$); $^{13}\text{C-NMR}$ (CDCl_3 , 0°C) δ 275.7 ($2\mathbf{a}$, CTol), 275.0 ($2\mathbf{b}$, CTol), 224.0 ($2\mathbf{b}$, CO), 223.4 ($2\mathbf{a}$, CO), 142.9 ($2\mathbf{a}$, $2\mathbf{b}$, $\text{C}_{ipso}\text{-Tol}$), 138.8 ($2\mathbf{a}$, $2\mathbf{b}$, $\text{C}_o\text{-Tol}$), 128.96, 128.92, 128.90, 128.78 ($2\mathbf{a}$, $2\mathbf{b}$, C_o & $\text{C}_m\text{-Tol}$), 60.3 ($2\mathbf{a}$, $\text{CH}_2\text{-tmeda}$), 60.1 ($2\mathbf{b}$, $\text{CH}_2\text{-tmeda}$), 57.0 ($2\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 56.8 ($2\mathbf{b}$, $\text{CH}_3\text{-tmeda}$), 52.8 ($2\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 51.5 ($2\mathbf{b}$, $\text{CH}_3\text{-tmeda}$); IR (KBr pellet) $\nu(\text{CO})$ 1984(s) 1911(s), 1888(s) cm^{-1} ; MS (70 eV) m/z 424 ($\text{M}^+\text{-CO}$). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2\text{BrMo}$: C, 42.6; H, 5.14; N, 6.21. Found: C, 43.4; H, 5.45; N, 6.27.

Preparation of $\text{Br}(\text{CO})_2(\text{tmeda})\text{W}=\text{CTol}$. A petroleum ether solution (200 mL) of $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Tol}$ (1.0 g, 2.2 mmol) was treated with BBr_3 (2.8 mL of 1.0 M solution in hexane) and the reaction mixture was stirred for 1 h. The supernatant was decanted off, the yellow residue, $\text{Br}(\text{CO})_4\text{W}=\text{CTol}$, was washed with petroleum ether (3 \times 20 mL) at -20°C . After evaporation of solvent *in vacuo*, the yellow solid was dissolved in dichloromethane (150 mL) at -20°C and TMEDA (1.7 mL, 11 mmol) was added. The temperature was slowly raised to 35°C and the solution was stirred for 1.5 h. After evaporation of the solvent *in vacuo*, the residue was washed with petroleum ether and was recrystallized with a mixture of chloroform and diethylether to give orange-yellow needles (3, 0.89 g, 1.65 mmol, 74%, $3\mathbf{a} : 3\mathbf{b} = 4.3 : 1$): $^1\text{H-NMR}$ (CDCl_3 , 25°C) δ 7.23-7.00 (m, 8H, $3\mathbf{a}$, $3\mathbf{b}$, C_6H_4), 3.21 (s, 6H, $3\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 3.17 (s, 6H, $3\mathbf{b}$, $\text{CH}_3\text{-tmeda}$), 2.99 (s, 6H, $3\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 2.90 (s, 4H, $3\mathbf{a}$, $\text{CH}_2\text{-tmeda}$), 2.88 (s, br, 10H, $3\mathbf{b}$, CH_3 , $\text{CH}_2\text{-tmeda}$), 2.25 (s, 6H, $3\mathbf{a}$, $3\mathbf{b}$, $\text{CH}_3\text{-Tol}$), $^{13}\text{C-NMR}$ (CDCl_3 , 25°C) δ 263.0 ($3\mathbf{b}$, CTol), 262.9 ($3\mathbf{a}$, CTol), 221.0 ($3\mathbf{b}$, CO), 220.4 ($3\mathbf{a}$, CO , $J_{\text{CW}} = 173.3$ Hz), 145.8 ($3\mathbf{a}$, $3\mathbf{b}$, $\text{C}_{ipso}\text{-Tol}$), 137.9 ($3\mathbf{a}$, $3\mathbf{b}$, $\text{C}_o\text{-Tol}$), 129.3, 129.2, 128.7, 128.6 ($3\mathbf{a}$, $3\mathbf{b}$, C_o & $\text{C}_m\text{-Tol}$), 61.1 ($3\mathbf{a}$, $\text{CH}_2\text{-tmeda}$), 61.0 ($3\mathbf{b}$, $\text{CH}_2\text{-tmeda}$), 58.4 ($3\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 58.1 ($3\mathbf{b}$, $\text{CH}_3\text{-tmeda}$), 53.4 ($3\mathbf{a}$, $\text{CH}_3\text{-tmeda}$), 52.1 ($3\mathbf{b}$, $\text{CH}_3\text{-tmeda}$), 21.6 ($3\mathbf{a}$, $3\mathbf{b}$, $\text{CH}_3\text{-Tol}$); IR (KBr pellet) $\nu(\text{CO})$ 1974(s), 1881(s), 1855(sh) cm^{-1} ; MS (70 eV) m/z 538 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2\text{BrW}$: C, 35.6; H, 4.30; N, 5.20. Found: C, 35.9; H, 4.59; N, 5.08.

Table 1. Crystal Data for $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}=\text{CTol}$ (1a)

Formula	$\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2\text{BrCr}$
<i>f</i> _w	407.27
Cryst syst	triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	12.792(2)
<i>b</i> , Å	13.400(5)
<i>c</i> , Å	11.645(4)
α , deg	101.26(2)
β , deg	103.04(2)
γ , deg	91.88(2)
<i>V</i> , Å ³	1907(1)
<i>Z</i>	2
ρ (calcd), gcm^{-3}	1.418
temp, K	295
$\lambda(\text{MoK}\alpha)$, Å	0.71069
μ , cm^{-1}	26.25

X-ray Data Collection and Structure Solution of

1a. Crystals of **1a** suitable for an X-ray analysis were obtained by slow recrystallization from methanol solution at -10°C . An opaque dark red crystal of approximate dimensions of $0.2 \times 0.4 \times 0.2$ mm was mounted and aligned on a CAD-4 diffractometer. Details of the relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 25 reflections with $10^\circ < \theta < 15^\circ$. Space group $P\bar{1}$ was determined from successful solution and refinement of structure; 3766 independent reflections in range $-16 \leq h \leq 16$, $0 \leq k \leq 15$, $-15 \leq l \leq 15$ were collected using graphite-monochromated Mo $K\alpha$ radiation and $\omega/2\theta$ scan mode. ω -scan width = $(0.8 + 0.35 \tan \theta)^\circ$, $\theta_{\text{max}} = 24^\circ$. One orientation reflections, 0 -2 -3, was checked every 200 seconds, and three standard reflections, 0 -2 -3, 4 0 2, -1 5 1, were monitored every 6000 seconds. These showed significant intensity variation (ca. 20%) during data collection; the decay correction was applied to the data¹¹. All data were converted to E_o values following correction for L-P and absorption factors. The four heavy atoms were located by using direct method^{11,12}, and all non-hydrogen atoms were found on subsequent difference Fourier maps, but there was some difficulty in finding C(2) and C(2)' atoms. Hydrogen atoms were put in calculated positions with a bond distance of 1.08 Å. They were used with the isotropic temperature factor $U_{11} = 0.05$ in a full-matrix least squares refinement with the program SHELX¹³ and function minimized was $\Sigma \omega(|F_o| - |F_c|)^2$, where $\omega = 1.0/(\sigma^2(F_o) + 0.001834F_o^2)$. Neutral atomic scattering factors were used with Br and Cr (f' and f'') corrected for anomalous dispersion¹⁴. Number of parameters refined was 397. Final reliability factors were $R = 0.0977$, $\omega R = 0.0977$, with average $\Delta/\sigma = 0.003$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.6/-0.5$ $\text{e}\text{\AA}^{-3}$ in final $\Delta\rho$ map and $S = 5.9106$. Final positional parameters and U_{ij} for non-hydrogen atoms are given in Table 2. Geometric calculations on the crystal and molecular structure were done using GEOM program¹⁵. All computations were carried out using the VAX computer at Chungnam National University.

Results and Discussion

Table 2. Final Positional Parameters ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with esd's for $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$ (**1a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U^{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U^{eq}
Molecule A					Molecule A'				
Br	3006(5)	1046(5)	4700(6)	139	Br'	8559(5)	1947(5)	10605(5)	139
Cr	4301(6)	2250(7)	3556(7)	80	Cr'	9281(6)	2213(6)	8407(7)	64
C(1)	3100(4)	3978(3)	5316(4)	160	O(1)'	8843(3)	4387(3)	9466(3)	124
C(2)	2740(3)	2212(4)	2041(4)	148	O(2)'	7067(3)	2009(3)	8125(4)	126
N(1)	5251(3)	940(3)	2309(3)	84	N(1)'	9759(3)	639(3)	7796(3)	79
N(2)	5478(4)	2237(4)	4614(4)	139	N(2)'	10942(3)	2289(3)	8629(3)	72
C(1)	3608(5)	3262(4)	4783(6)	143	C(1)'	9032(5)	3411(6)	8957(4)	149
C(2)	3365(3)	2246(5)	2702(3)	124	C(2)'	7968(2)	2041(5)	8289(5)	126
C(3)	5620(4)	1158(3)	1135(4)	102	C(3)'	8974(4)	-113(3)	8300(4)	105
C(4)	4550(4)	17(4)	2122(5)	136	C(4)'	9869(5)	271(4)	6506(4)	139
C(5)	6145(6)	877(6)	2959(6)	176	C(5)'	10794(3)	601(4)	8095(7)	180
C(6)	6051(5)	1386(8)	4036(6)	250	C(6)'	11473(4)	1310(6)	8167(6)	162
C(7)	5170(5)	2068(4)	5889(4)	149	C(7)'	11062(3)	2680(4)	9858(4)	83
C(8)	6240(4)	3090(4)	4642(5)	187	C(8)'	11609(3)	3006(4)	7894(4)	102
C	4781(3)	3242(3)	2843(4)	79	C'	9508(3)	2570(4)	7135(4)	79
CP(1)	5000(4)	4165(4)	2317(3)	79	CP(1)'	9416(3)	3012(3)	6072(4)	58
CP(2)	6070(4)	4358(3)	1674(4)	84	CP(2)'	10123(4)	2687(4)	4873(5)	108
CP(3)	6176(4)	5196(4)	1207(4)	81	CP(3)'	9972(6)	3199(5)	3915(4)	132
CP(4)	5426(4)	5968(5)	1210(4)	102	CP(4)'	9215(5)	3946(5)	3974(8)	121
CP(5)	4360(5)	5719(3)	1849(4)	105	CP(5)'	8681(4)	4256(5)	5172(6)	122
CP(6)	4145(3)	4819(4)	2326(4)	103	CP(6)'	8707(3)	3763(4)	6167(3)	63
CM	5560(4)	6845(3)	682(5)	119	CM'	9213(5)	4388(4)	2923(3)	121

$U_{eq} = [1/3(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cos\beta \cos\gamma)](U_{11} \sin^2\alpha + U_{22} \sin^2\beta + U_{33} \sin^2\gamma + 2U_{12} \sin\alpha \sin\beta \cos\gamma + 2U_{13} \sin\alpha \sin\gamma \cos\beta + 2U_{23} \sin\beta \sin\gamma \cos\alpha)$

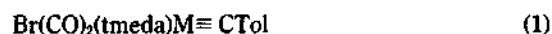
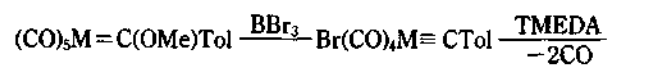
Synthesis and Characterization of 1, 2, and 3. The *trans*-halotetracarbonyl metal alkylidyne complexes $\text{X}(\text{CO})_4\text{M}\equiv\text{CR}$ have been generally prepared from alkoxy alkylidene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OR})\text{R}$ via alkoxide abstraction from alkylidene carbon atoms by a variety of Lewis acid (BX_3)^{9a}. The usefulness of *trans*- $\text{X}(\text{CO})_4\text{M}\equiv\text{CR}$ complexes is somewhat limited as a basis for general investigations of alkylidyne chemistry due to their thermal instability. Stable complexes $\text{X}(\text{CO})_2\text{L}_2\text{M}\equiv\text{CR}$, however, can be obtained by substitution of two carbonyl ligands with donor ligands (L) such as phosphines, phosphites and nitrogen donor molecules^{8,9}. The nitrogenous ligands have proven particularly useful, because the amine-substituted products possess improved thermal stability and show coordinative lability for further substitution reactions⁸.

Mayr and co-workers have recently reported synthesis of various TMEDA-substituted alkylidyne complexes by reaction of acyl complexes $[\text{NMe}_2][(\text{CO})_5\text{M}(\text{O})\text{R}]$ at low temperatures with a variety of carbon-based Lewis acids and subsequent treatment with TMEDA⁸. They have obtained a single isomer of $\text{X}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CPh}$ ($\text{X}=\text{Cr}$, $\text{M}=\text{Cr}$, Mo , W) complexes and assumed its structure to be that previously proposed for *trans, cis*- $\text{Br}(\text{CO})_2(\text{py})_2\text{W}\equiv\text{CPh}$ complex^{9b} containing the bromide *trans* to the alkylidyne ligand with the two respective pyridine and carbonyl ligands *cis* to each other.

The alkylidene complexes, *trans*- $\text{Br}(\text{CO})_4\text{M}\equiv\text{CTol}$ ($\text{M}=\text{Cr}$, Mo , W), have been similarly prepared from the reaction of

$(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{Tol}$ and BBr_3 , and used *in situ* for the preparation of TMEDA-substituted complexes $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CTol}$ as shown in Eq. (1). We have, however, obtained two isomers of $\text{Br}(\text{CO})_2(\text{tmeda})\text{M}\equiv\text{CTol}$ complexes, whose ratios depend upon the metals used as is indicated in Eq. (1). The ^1H and ^{13}C -NMR spectra of **1**, **2** and **3** exhibit respective two sets of resonances for two isomers, and typical NMR spectra of complex **1** (**1a** and **1b**) are shown in Figure 1. The isomer ratios have been determined by integration of NMR signals for each isomer, respectively. In Scheme 1 are shown four possible structures for complex **1**, diastereomer **1a-1d**.

When a methanol solution of **1** is allowed to induce slow recrystallization at -10°C , it crystallizes as pure *trans, cis*-diastereomer **1a**, which has been characterized by a single crystal X-ray diffracton study (vide infra). The structure of the second isomer is determined based on NMR and IR spectroscopic data. The two equivalent carbonyl ligand in both **1a** and **1b** would show a single resonance in the respective ^{13}C -NMR spectrum, whereas those in **1c** and **1d** are not equi-



- 1** : $\text{M}=\text{Cr}$, 76% (**1a** : **1b** = 1 : 1.1)
2 : $\text{M}=\text{Mo}$, 56% (**2a** : **2b** = 1 : 6.6)
3 : $\text{M}=\text{W}$, 74% (**3a** : **3b** = 4.3 : 1)

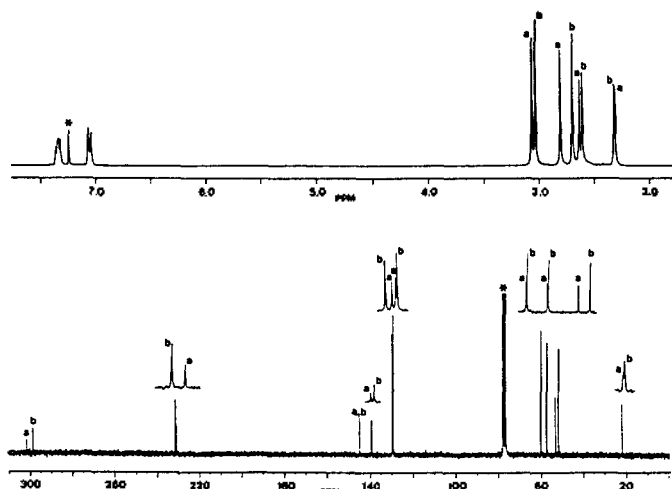
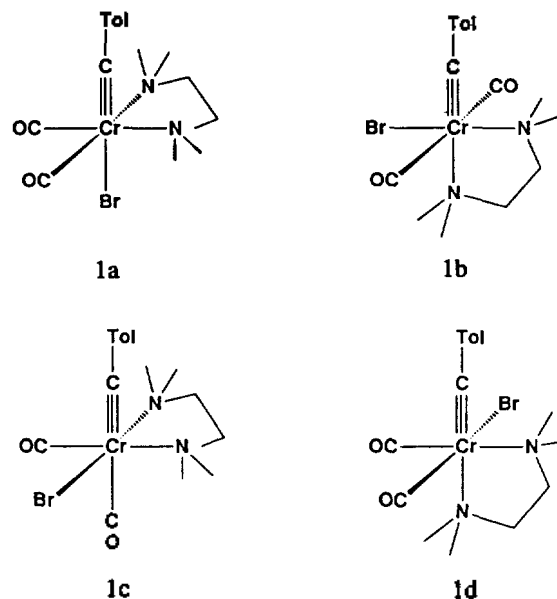


Figure 1. ^1H -NMR (300 MHz, CDCl_3 , upper, $1\text{a} : 1\text{b} = 1 : 1.1$) and ^{13}C -NMR (75 MHz, CDCl_3 , lower, $1\text{a} : 1\text{b} = 1 : 2$) spectra of a mixture of 1a and 1b . The solvent peaks are labelled with asterisks.



Scheme 1.

Table 3. Characteristic ^{13}C -NMR Data for Alkylidyne complexes $1\text{a}-3\text{b}$

Compound	$\delta(\text{CTol})$	$\delta(\text{CO})$	ppm
$\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$, 1a	301.1	230.4	
1b	298.2	230.9	
$\text{Br}(\text{CO})_2(\text{tmeda})\text{Mo}\equiv\text{CTol}$, 2a	275.7	223.4	
2b	275.0	224.0	
$\text{Br}(\text{CO})_2(\text{tmeda})\text{W}\equiv\text{CTol}$, 3a	262.9	220.4 ($J_{\text{CW}} = 173.3$ Hz)	
3b	263.0	221.0	

Table 4. Carbonyl Stretching Bands (ν_{CO}) of Alkylidyne Complexes $1\text{a}-3\text{b}$

Compound	ν_{sym}	ν_{asym} (cm^{-1})
$\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}$, 1a	1993	1921
1b		1903
$\text{Br}(\text{CO})_2(\text{tmeda})\text{Mo}\equiv\text{CTol}$, 2a	1984	1911
2b		1888
$\text{Br}(\text{CO})_2(\text{tmeda})\text{W}\equiv\text{CTol}$, 3a	1974	1881
3b		1855

valent and would exhibit two distinct resonances. The two carbonyl ligands in **1b** are *trans* to each other and would show a single carbonyl absorption band (ν_{CO}) in the IR spectrum. However, those in the other three diastereomers (**1a**, **1c**, and **1d**) are in a *cis* position and would reveal two ν_{CO} peaks (ν_{sym} and ν_{asym})²⁴, respectively.

The ^{13}C -NMR and IR spectra of a mixture of **1a** and the second isomer show two carbonyl resonances and three carbonyl stretching bands as summarized in Tables 3 and 4, respectively. These results unambiguously indicate that structure of the second isomer is that of *cis, trans-1b* in Scheme 1. Structures for the molybdenum (**2a** and **2b**) and tungsten (**3a** and **3b**) analogues have been similarly assigned.

The methyl and methylene resonances of the *tmeda* ligand of **a** isomers appear consistently more downfield than those of **b** isomers in both ^1H and ^{13}C -NMR spectra (see Experimental Section). Nevertheless, the chemical shifts of both alkylidyne and carbonyl carbon resonances do not reveal a regular trend for the two isomers **a** and **b** (see Table 3). Each IR spectrum of a mixture of **a** and **b** isomers shows three ν_{CO} bands, two of which are assigned to **a** isomers and the lowest energy band to **b** isomers as shown in Table 4. Pure compounds of **1a**, **2a**, and **3a** can be obtained by slow fractional recrystallization at low temperatures (≤ -10 °C) from respective mixtures of two diastereomers. However, rapid or prolonged recrystallization results in contamination of pure **a** isomer by isomer **b**. It has not been successful to isolate pure samples of **b** diastereomers, because the supernatants always contain some of **a** isomers even after fractional recrystallization of **a** isomers. The two diastereomers, **a** and **b**, are not interconvertible in solution. The isomer **a**, however, undergoes isomerization to **b** in the presence of excess *TMEDA* in CDCl_3 at room temperature, when monitored by ^1H -NMR spectroscopy. Thermal instability of the complexes at room temperature in solution precludes the detailed study of the isomerization reaction.

Molecular Structure of *trans, cis-1a*. The crystallographic asymmetric unit contains two molecules, "A" and "A'". The overall molecular geometry and the scheme used for labelling atoms are illustrated in Figure 2. A stereoview of the molecule and a stereoscopic view of the crystal packing drawn by ORTEP¹⁶ are shown in Figures 3 and 4, respectively. Interatomic distances and angles are collected in Tables 5 and 6.

The geometry of complex **1a** is found to be octahedral with the bromide ligand *trans* to the alkylidyne carbon, the two *cis*-carbonyl ligands, and the bidentate *TMEDA* ligand. The average $\text{Cr}\equiv\text{C}$ (alkylidyne) distance in **1a** is 1.667 (10) Å. We note here that the following $\text{Cr}\equiv\text{C}$ (alkylidyne) distances have been observed in chromium alkylidyne clusters which are associated with carbonyl and a bromide ligands: 1.67

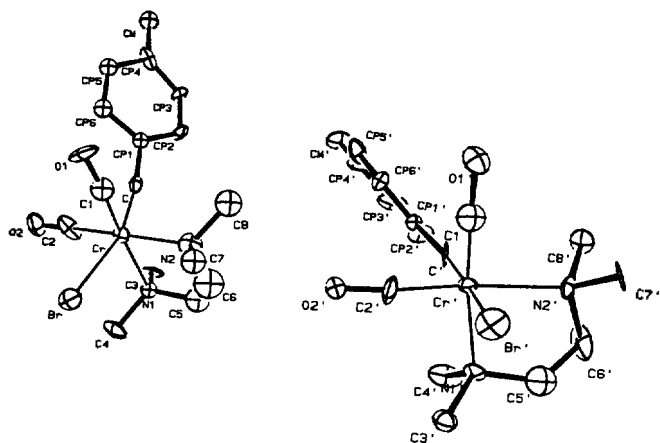


Figure 2. Molecular geometry and atomic labelling scheme for $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}(\mathbf{1a})$.

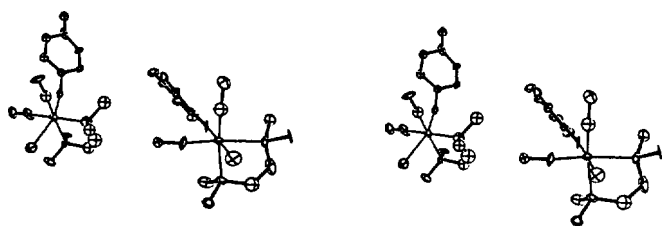


Figure 3. Stereoview of $\mathbf{1a}$.

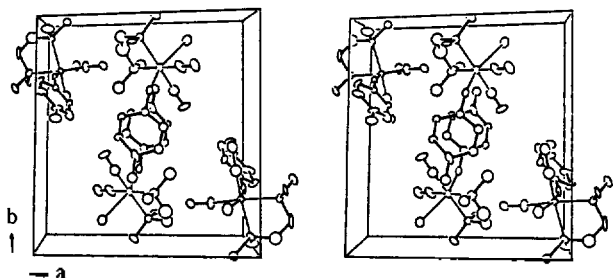


Figure 4. Stereoview of a unit cell packing for $\mathbf{1a}$. Origin, lower left; c -axis, horizontal; b -axis, vertical.

Table 5. Interatomic Distances (Å) and Esd's for $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}(\mathbf{1a})$

	Molecule A	Molecule A'
Cr-C	1.727(10)	1.607(9)
Cr-Br	2.607(9)	2.608(9)
Cr-N(1)	2.240(33)	2.152(36)
Cr-N(2)	2.152(51)	2.194(37)
Cr-C(1)	1.848(10)	1.621(11)
Cr-C(2)	1.720(8)	1.720(8)
O(1)-C(1)	1.164(7)	1.332(8)
O(2)-C(2)	1.223(5)	1.208(4)
N(1)-C(3)	1.426(5)	1.506(6)
N(1)-C(4)	1.514(7)	1.463(5)
N(1)-C(5)	1.520(8)	1.448(6)
N(2)-C(6)	1.350(11)	1.446(8)
N(2)-C(7)	1.507(6)	1.465(6)
N(2)-C(8)	1.478(8)	1.524(6)
C(5)-C(6)	1.287(10)	1.270(8)
C-CP(1)	1.476(6)	1.501(6)
CP(1)-CP(2)	1.446(7)	1.475(7)
CP(2)-CP(3)	1.331(6)	1.469(7)
CP(3)-CP(4)	1.433(7)	1.397(9)
CP(4)-CP(5)	1.461(8)	1.396(7)
CP(5)-CP(6)	1.418(7)	1.448(8)
CP(1)-CP(6)	1.421(7)	1.349(6)
CP(4)-CM	1.418(7)	1.461(9)

Å in $\text{Br}(\text{CO})_4\text{Cr}\equiv\text{CC}_{10}\text{H}_{19}$ (menthyl)¹⁷, 1.68(2) Å in $\text{Br}(\text{CO})_4\text{Cr}\equiv\text{CC}_6\text{H}_4\text{CF}_3$ ^{18a}, 1.69(4) Å in $\text{Br}(\text{CO})_3(\text{PMe}_3)\text{Cr}\equiv\text{CMe}$ ¹⁸, 1.71(2) Å in $\text{Br}(\text{CO})_4\text{Cr}\equiv\text{C}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)$ ¹⁹, 1.72(1) Å in $\text{Br}(\text{CO})_4\text{Cr}\equiv\text{CNET}_2$ ²⁰, and 1.84(2) Å in $\text{Br}(\text{CO})_2(\text{py})_2\text{W}\equiv\text{CPh}$ ^{2b}. The average Cr-Br length in $\mathbf{1a}$, 2.608(9) Å, compares with the average distance of 2.57 Å in the above six alkyldiene compounds reported. A distinct bend (av. 174°) of $\text{Cr}\equiv\text{C}-\text{C}$ atoms has been observed in the previous complexes and the present complex $\mathbf{1a}$ reveals $\langle\text{Cr}-\text{C}-\text{CP}(1)\rangle = 167.2(4)^\circ$. The

Table 6. Selected Interatomic Angles(deg) with Esd's for $\text{Br}(\text{CO})_2(\text{tmeda})\text{Cr}\equiv\text{CTol}(\mathbf{1a})$

	Molecule A	Molecule A'		Molecule A	Molecule A'
N(1)-Cr-Br	92.3(1)	91.9(1)	C(6)-N(2)-Cr	101.9(4)	110.6(3)
N(2)-Cr-Br	93.7(2)	91.7(1)	C(7)-N(2)-Cr	121.7(4)	114.9(3)
N(1)-Cr-N(1)	85.0(2)	79.5(1)	C(7)-N(2)-C(6)	102.3(6)	110.3(4)
C(1)-Cr-Br	83.9(1)	83.5(2)	C(8)-N(2)-Cr	116.8(4)	111.5(3)
C(1)-Cr-N(1)	170.4(2)	173.2(3)	C(8)-N(2)-C(6)	107.1(6)	104.7(4)
C(1)-Cr-N(2)	86.4(3)	94.3(2)	C(8)-N(2)-C(7)	105.1(4)	104.1(4)
C(2)-Cr-Br	86.1(2)	84.6(2)	O(1)-C(1)-Cr	162.8(6)	176.8(6)
C(2)-Cr-N(1)	94.3(2)	96.1(2)	O(2)-C(2)-Cr	176.4(5)	172.3(5)
C(2)-Cr-N(2)	179.3(3)	174.2(2)	C(6)-C(5)-N(1)	119.1(6)	127.5(5)
C(2)-Cr-C(1)	94.2(3)	89.9(3)	C(5)-C(6)-N(2)	130.9(6)	110.0(4)
C-Cr-Br	161.8(1)	166.9(2)	CP(1)-C-Cr	170.0(4)	164.6(3)
C-Cr-N(1)	100.9(2)	99.1(2)	CP(2)-CP(1)-C	120.4(5)	122.4(4)
C-Cr-N(2)	98.7(2)	96.8(2)	CP(6)-CP(1)-C	120.4(4)	121.8(4)
C-Cr-C(1)	84.3(2)	82.8(2)	CP(6)-CP(1)-CP(2)	118.8(4)	115.8(4)

C-Cr-C(2)	81.9(3)	87.0(2)	CP(3)-CP(2)-CP(1)	115.7(4)	117.0(5)
C(3)-N(1)-Cr	110.0(3)	115.4(3)	CP(4)-CP(3)-CP(2)	132.4(5)	128.5(6)
C(4)-N(1)-Cr	110.8(3)	114.3(3)	CP(5)-CP(4)-CP(3)	109.2(5)	108.4(8)
C(4)-N(1)-C(3)	104.1(4)	100.9(4)	CM-CP(4)-CP(5)	131.1(5)	120.3(7)
C(5)-N(1)-C(3)	113.6(4)	113.3(4)	CM-CP(4)-CP(5)	119.6(6)	130.4(6)
C(5)-N(1)-Cr	99.7(3)	103.6(3)	CP(6)-CP(5)-CP(4)	123.0(5)	127.2(6)
C(5)-N(1)-C(3)	113.6(4)	113.3(4)	CP(5)-CP(6)-CP(1)	120.3(4)	122.1(4)
C(5)-N(1)-C(4)	117.8(5)	109.6(5)			

two molecules (A and A') are essentially equivalent in terms of both connectivity and ligand conformation. The only conformational difference between the two molecules is that the torsion angle of N(1)-C(5)-C(6)-N(2) in the ethylene group is \pm gauche, 34.9° and -24.8° for A and A' molecules, respectively. The crystal consists of discrete molecular units that are mutually separated by normal van der Waals' contacts with the shortest intermolecular distances 3.366(7) Å between C(4) and O(2)' at (x, y, 1-z).

All other features are in the expected ranges, but are of relatively low accuracy due to poor crystal quality. It is, therefore, perhaps not fruitful to undertake a detailed discussion of the individual bond length and angle.

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