Inorganica Chimica Acta, *156* (1989) 179–181

1,4-Diaza-1,3-butadiene Seven-coordinate Complexes of Molybdenum(II) and Tungsten(II)

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(Received February 19, 1988)

Abstract

The seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with an equimolar quantity of RN:CHCH:NR (R = Bu^i, Cy, Ph or *p*-MeOPh) in CH_2Cl_2 at room temperature to afford good yields of the new 1,4-diaza-1,3-butadiene complexes $[MI_2(CO)_3(RN:CHCH:NR)]$ (1–8) by the successive substitution of two acetonitrile ligands. The new complexes 1–8 were characterised by elemental analysis (C, H and N), infrared and ^1H NMR spectroscopy.

Introduction

1,4-Diaza-1,3-butadienes which contain the α-diimine moiety, –N=C–C=N– have often been used as ligands in organometallic chemistry [1–8]. It has been observed [9] that they have similar donor properties to the extensively studied 2,2′-bipyridyl and 1,10-phenanthroline bidentate nitrogen donor ligands. Several seven-coordinate complexes of molybdenum(II) or tungsten(II) have been reported containing 1,4-diaza-1,3-butadienes as attached ligands. For example, in 1985 Bell and Walton [10] reported the reactions of $[M(CO)_4(RN:CHCH:NR)]$ (M = Mo or W; R = Pr^i, Bu^t or Cy) with $SnCl_4$ in CH_2Cl_2 afford the seven-coordinate complexes $[MCl(SnCl_3)(CO)_3(RN:CHCH:NR)]$ in good yield. They also found that the molybdenum complexes $[MoCl(SnCl_3)(CO)_3(RN:CHCH:NR)]$ (R = ^iPr or Cy) reacted with an excess of R′NC (R′ = $CHMe_2$, CMe_3 or Cy) in the presence of $K[PF_6]$ to give either mono or dicationic complexes of the type $[MoCl(CNR')_4(RN:CHCH:NR)][PF_6]$ or $[Mo(CNR')_5(RN:CHCH:NR)][PF_6]_2$.

In recent years we have been investigating the chemistry of the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) which are prepared in quantitative yield by reacting the zerovalent compounds $[M(CO)_3(NCMe)_3]$ with one equivalent of I_2 at 0 °C [11]. In this paper we describe the reactions of these complexes with 1,4-diaza-1,3-butadienes.

Experimental

All reactions described in this paper were carried out using standard Schlenk line techniques. The bisacetonitrile compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were synthesised by the literature method [11]. The 1,4-diaza-1,3-butadienes, RN:CHCH:NR (R = Bu^i, Cy, Ph or *p*-MeOPh) were also prepared by standard published procedures [12–16]. CH_2Cl_2 was dried and distilled before use.

Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. ^1H NMR spectra were recorded on a Jeol FX 60 NMR spectrometer (all spectra were calibrated against tetramethylsilane).

$MoI_2(CO)_3(Bu^iN:CHCH:NBu^i)$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.41 g, 0.802 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $Bu^iN:CHCH:NBu^i$ (0.135 g, 0.802 mmol) and the mixture was stirred for 20 min. After filtration, removal of the solvent *in vacuo* gave red crystals of $[MoI_2(CO)_3(Bu^iN:CHCH:NBu^i)]$ (yield = 0.32 g, 66%) which were recrystallised from CH_2Cl_2.

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with $Bu^iN:CHCH:NBu^i$ afforded the complex $[WI_2(CO)_3(Bu^iN:CHCH:NBu^i)]$ (2).

$MoI_2(CO)_3(CyN:CHCH:NCy)$ (3)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.34 g, 0.66 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added CyN:CHCH:NCy (0.143 g, 0.65 mmol) and the mixture was stirred for 15 min. After filtration, removal of the solvent *in vacuo* gave purple–black crystals of $[MoI_2(CO)_3(CyN:CHCH:NCy)]$ (yield = 0.26 g, 60%) which were recrystallized from CH_2Cl_2.

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0020-1693/89/$3.50

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TABLE 1. Physical and Analytical Data[a] for the Complexes [MI$_2$(CO)$_3$(RN:CHCH:NR)]

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
1 [MoI$_2$(CO)$_3$(Bu^{i}N:CHCH:NBu^i)]	red	66	26.4(25.9)	4.3(3.4)	4.5(4.7)
2 [WI$_2$(CO)$_3$(Bu^{i}N:CHCH:NBu^i)]	brown	81	23.0(22.6)	3.3(2.9)	3.9(4.1)
3 [MoI$_2$(CO)$_3$(CyN:CHCH:NCy)]	purple	60	30.5(31.2)	4.0(3.7)	4.2(4.3)
4 [WI$_2$(CO)$_3$(CyN:CHCH:NCy)]	red	62	27.8(27.5)	3.9(3.5)	3.8(3.8)
5 [MoI$_2$(CO)$_3$(PhN:CHCH:NPh)]	green–brown	47	27.4(28.0)	2.0(1.7)	3.6(3.8)
6 [WI$_2$(CO)$_3$(PhN:CHCH:NPh)]	purple	76	31.5(31.8)	2.6(1.9)	4.2(4.4)
7 [MoI$_2$(CO)$_3$(*p*-MeOPhN:CHCH:NPhOMe-*p*)]	green	53	32.1(32.5)	2.6(2.3)	4.1(4.0)
8 [WI$_2$(CO)$_3$(*p*-MeOPhN:CHCH:NPhOMe-*p*)]	red–brown	64	29.0(28.9)	2.5(2.0)	3.5(3.6)

[a]Calculated values in parentheses.

A similar reaction of [WI$_2$(CO)$_3$(NCMe)$_2$] with CyN:CHCH:NCy afforded the complex [WI$_2$(CO)$_3$(CyN:CHCH:NCy)] (4).

WI$_2$(CO)$_3$(PhN:CHCH:NPh) (6)

To [WI$_2$(CO)$_3$(NCMe)$_2$] (0.41 g, 0.68 mmol) with continuous stirring under a stream of dry nitrogen was added PhN:CHCH:NPh (0.14 g, 0.68 mmol), and the mixture was stirred for 15 min. After filtration, removal of the solvent *in vacuo* gave purple–red crystals of [WI$_2$(CO)$_3$(PhN:CHCH:NPh)] (yield = 0.39 g, 76%) which were recrystallised from CH$_2$Cl$_2$.

A similar reaction of [MoI$_2$(CO)$_3$(NCMe)$_2$] with PhN:CHCH:NPh afforded the complex [MoI$_2$(CO)$_3$(PhN:CHCH:NPh)] (5).

WI$_2$(CO)$_3$(p-MeOPhN:CHCH:NPhOMe-p) (8)

To [WI$_2$(CO)$_3$(NCMe)$_2$] (0.41 g, 0.68 mmol) with continuous stirring under a stream of dry nitrogen was added *p*-MeOPhN:CHCH:NPhOMe-*p* (0.161 g, 0.68 mmol), and the mixture was stirred for 20 min. After filtration, removal of the solvent *in vacuo* gave red–brown crystals of [WI$_2$(CO)$_3$(*p*-MeOPhN:CHCH:NPhOMe-*p*)] (yield 0.34 g, 64%), which were recrystallised from CH$_2$Cl$_2$.

TABLE 2. Infrared Data[a] for the Complexes [MI$_2$(CO)$_3$(RN:CHCH:NR)]

Complex	ν(CO) (cm^{-1})	ν(C=N) (cm^{-1})
1	2060(m), 2000(s), 1939(s)	1622(s)
2	2061(m), 1998(s), 1921(s)	1630(m)
3	2025(m), 1979(s), 1935(s)	1518(m)
4	2018(m), 1976(s), 1922(s)	1582(m)
5	2020(m), 1970(s), 1941(s)	1589(m)
6	2062(m), 2001(s), 1921(s)	1599(s)
7	2038(m), 1978(s), 1941(s)	1600(m)
8[b]	2010(s), 1952(s), 1918(s)	1659(m)

[a]Spectra recorded in CHCl$_3$; m, medium; s, strong. [b]Spectrum recorded in MeOH.

A similar reaction of [MoI$_2$(CO)$_3$(NCMe)$_2$] with *p*-MeOPhN:CHCH:NPhOMe-*p* afforded the complex [MoI$_2$(CO)$_3$(*p*-MeOPhN:CHCH:NPhOMe-*p*)] (7).

Results and Discussion

Equimolar quantities of [MI$_2$(CO)$_3$(NCMe)$_2$] (M = Mo or W) and RN:CHCH:NR (R = Bu^i, Cy, Ph or *p*-MeOPh) react in CH$_2$Cl$_2$ at room temperature to give the acetonitrile substituted products [MI$_2$(CO)$_3$(RN:CHCH:NR)] (1–8) in good yield. The complexes were characterised by elemental analysis (C, H and N) (Table 1), infrared spectroscopy (Table 2) and ^{1}H NMR spectroscopy (Table 3).

TABLE 3. ^{1}H NMR Data[a] for the Complexes [MI$_2$(CO)$_3$(RN:CHCH:NR)]

Complex	^{1}H NMR data (δ (ppm))
1	1.12(d, J = 14.4 Hz, 12H, CH_3), 2.48 (brm, 2H, CH), 3.5(d, J = 7.2 Hz, 4H, CH$_2$), 8.45(s, 2H, =CH)
2	1.15(d, J = 5.9 Hz, 12H, CH_3), 2.45(brm, 2H, CH), 3.51(brd, J = 2.9 Hz, 4H, CH_2), 8.36(s, 2H, =CH)
3	1.67(brm, 22H, *Cy*), 8.85(s, 2H, =CH)
4	1.73(brm, 22H, *Cy*), 8.63(s, 2H, =CH)
5	7.16(brm, 10H, Ph), 7.58(s, 2H, =CH)
6	7.38(brm, 10H, Ph), 8.06(s, 2H, =CH)
7	3.79(brs, 6H, OCH_3), 7.49, 6.9(brm, 8H, Ph), 8.33(s, 2H, =CH)
8	3.81, 3.88(s, 6H, OCH$_3$), 7.04, 6.9(brm, 4H, Ph), 7.48, 7.62(brm, 4H, Ph), 8.52(s, 2H, =CH)

[a]Spectra recorded in CDCl$_3$ (+25 °C) and referenced to Me$_4$Si.

The complexes **1–8** are stable in the solid state when they are stored under nitrogen. However, they decompose in solution when exposed to air. The compounds are all soluble in CH_2Cl_2 and $CHCl_3$, but only slightly soluble in diethylether.

It is likely that the reaction of $[MI_2(CO)_3(NCMe)_2]$ with RN:CHCH:NR proceeds via dissociation of the acetonitrile ligands from $[MI_2(CO)_3(NCMe)_2]$ since the complexes obey the effective atomic number rule and are highly crowded. Since the acetonitrile ligands in $[MI_2(CO)_3(NCMe)_2]$ are mainly σ-donor ligands they would be expected to be and were found to be labile in this system.

The infrared spectra of complexes **1–8** all show three carbonyl bands (Table 2), similar to other related seven-coordinate complexes of the type $[MX_2(CO)_3(LL)]$ (M = Mo or W; X = Cl, Br or I; LL = neutral bidentate ligand). The X-ray crystal structures of several of the complexes $[MX_2(CO)_3(LL)]$ have been determined [17–20] and have been found to have capped octahedral geometry. In view of the similar spectral properties of $[MI_2(CO)_3(RN{:}CHCH{:}NR)]$ (**1–8**) to other $[MX_2(CO)_3(LL)]$ complexes, it is likely that **1–8** will have capped octahedral geometry. Several unsuccessful attempts were made to grow crystals of **1–8** for X-ray crystallography. The resonances shown in the ^1H NMR spectra of **1–8** are as expected for 1,4-diaza-1,3-butadiene compounds.

Several attempts were made to prepare the bis-1,4-diaza-1,3-butadiene complexes $[MI(CO)_2(RN{:}CHCH{:}NR)_2]I$ or $[M(CO)_3(RN{:}CHCH{:}NR)_2]2I$ by reaction of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of RN:CHCH:NR in CH_2Cl_2. These reactions were not successful since the products of these reactions were highly unstable. However, reactions of the complexes $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of PPh_3 in CH_2Cl_2 to give $[MI_2(CO)_3(NCMe)(PPh_3)]$ (which have been isolated and fully characterised [21]) followed by an *in situ* reaction with one equivalent of RN:CHCH:NR gave cationic complexes of the type $[MI(CO)_3(PPh_3)(RN{:}CHCH{:}NR)]I$. Although the complexes are not very stable and it was difficult to obtain satisfactory analytical data for these compounds infrared and ^1H NMR spectroscopy confirmed the formation of these compounds. For example, the infrared spectrum of $[WI(CO)_3(PPh_3)(Bu^iN{:}CHCH{:}NBu^i)]I$ showed three carbonyl bands at $\nu(CO) = 2098(s)$, 1986(s) and 1958(s) cm^{-1} and $\nu(CN) = 1679(m)$. The room temperature ^1H NMR spectrum ($CDCl_3$) of $[WI(CO)_3(PPh_3)(Bu^iN{:}CHCH{:}NBu^i)]I$ showed resonances at $\delta = 1.13$(d, $J = 9.6$ Hz, 12H, CH_3), 2.45 (brm, 2H, CH), 3.48(brs, 4H, CH_2), 7.46(s, 15H, Ph) and 8.7(s, 2H, $=CH$).

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