Journal of Organometallic Chemistry, 383 (1990) 357–366
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20035

Carbonyl ligands from alkynes: oxidative decarbonation of acetylide bridged complexes

Wolfgang Bernhardt und Heinrich Vahrenkamp *

Institut für Anorganische und Analytische Chemie der Universität Freiburg, Albertstr. 21, D-7800 Freiburg (F.R.G.)

(Received February 15th, 1989)

Abstract

The organometal acetylides $Cp(CO)_2MC{\equiv}CR$ (**1**, M = Fe, R = Ph and **2**, M = Ru, R = Ph, t-Bu, Me) react with $Co_2(CO)_8$ to form the acetylide bridged trinuclear complexes $Co_2(CO)_6$-μ-$[Cp(CO)_2MC{\equiv}CR]$ (**3**, M = Fe, and **4**, M = Ru). Of these, the phenyl acetylide compounds undergo a non-destructive reaction with oxygen which results in the net loss of one carbon atom together with a CO ligand and the formation of the alkylidyne bridged clusters $Co_2MCp(CO)_7(\mu_3\text{-}CPh)$ (**5**, M = Fe, and **6**, M = Ru). The molecular structure of **6** has been determined by an X-ray analysis. The mechanism of the oxidation reaction has been elucidated by ^{13}C labelling of the acetylide α-C atom and EI mass spectrometry. It has been found that this C atom is converted to CO which, with a probability of 7/9, ends up as a CO ligand in the product cluster. This means that the oxidation converts the α-C to CO before elimination of the CO ligands.

Introduction

After one hundred years of metal carbonyl chemistry the focus of research is no longer on finding sources of CO or on making new simple metal carbonyls, but on using metal carbonyls or CO ligands to generate new bonding types or reactivity patterns in the ligand sphere [1]. Actually, new binary or ternary metal carbonyls have become extremely rare, two of the recent examples being $Os_4(CO)_{14}$ [2] and $RuCo_2(CO)_{11}$ [3]. Similarly, except for CO itself, few other compounds are useful as precursors of CO ligands [4]. Most of them contain the C–O linkage already, and as a rule the synthesis of a metal carbonyl is a reductive process. There should, however, be some potential in reactions which generate CO by oxidation of compounds containing metal–carbon bonds, and there exist demonstrations of the value of high oxidation state organometallic chemistry [5]. Along these lines we have

0022-328X/90/$03.50

undertaken a few investigations on the oxidative behaviour of polynuclear organometallic compounds.

Our investigations were triggered by the accidental observation that compound **4a**, mentioned below and containing an acetylide ligand, is not completely destroyed in air. We then started a comparative study of organometal acetylides as ligands for polynuclear complexes. This has resulted in several new structural types and ways of rearrangement for acetylide bridged tetranuclear clusters [6]. And it has revealed that terminal acetylenes, via the organometallic Fe and Ru acetylides, can serve as sources of CO resulting from acetylenic carbon atoms [7].

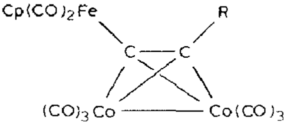
The work described herein is, in a way, a continuation of work by Yamazaki [8] and Bruce [9,10] who synthesized the mononuclear acetylides for the first time and found that they can be used as ligands for polynuclear metal carbonyl complexes.

Reactions

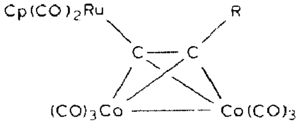
The well-known fact that the organometallic iron and ruthenium acetylides **1** and **2** [9] are good ligands for metal carbonyl complexes [8,10] was exploited here to obtain the trinuclear starting complexes **3a** and **4a**, **4b**, **4c** from reactions with $Co_2(CO)_8$. Of these, **3a** was known [8] and has been subjected to a crystal structure determination [10]. **4a**, **4b**, and **4c** are reported for the first time. All these reactions proceed easily and in good yields, just like the reactions of $Co_2(CO)_8$ with normal alkynes.

$Cp(CO)_2M—C\equiv CR$

	M	R
1a	Fe	Ph
2a	Ru	Ph
2b	Ru	t-Bu
2c	Ru	Me

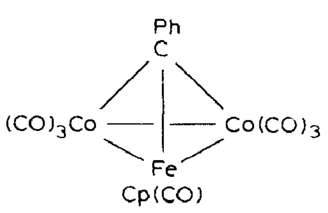


(3a)

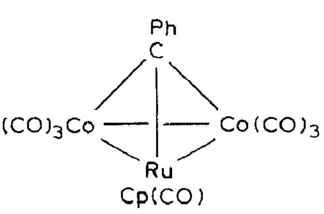


(4a: R = Ph ;
4b: R = t-Bu ;
4c: R = Me)

The products **3** and **4** show the typical nonpolar behaviour and air sensitivity of metal carbonyl derivatives. Uncontrolled exposure to air leads to complete destruction. In the case of **3a** and **4a**, however, there is an isolable primary oxidation product, which could not be observed in the case of **4b** and **4c**. The accidental observation of this product led to the optimization of the reaction conditions, finally giving above 50% yields of **5** and **6** in solution, and yields after recrystallization of 20 and 44%.



(5)



(6)

The best reagent for oxidation is pure oxygen bubbled through the solutions for short periods. It seems that **5** and **6** are the only oxidation products of **3a** and **4a**.

But they are more sensitive towards oxygen than their precursors which means that their concentration in solution starts falling before all **3a** or **4a** is used up. Alternative oxidants (Me_3NO, H_2O_2) gave only destructive reactions, while **5** and **6** could not be obtained by heating or photolyzing in the absence of oxygen or in the presence of water.

The transformations of **3a** and **4a** to **5** and **6** correspond to the net loss of one CO ligand and one carbon atom (the acetylide α-C atom). Passing the reaction gases in a stream of purified oxygen through $Ba(OH)_2$ and $PdCl_2$ solutions confirmed that during the conversion both CO and CO_2 are formed. This was, however, also the case when **5** or **6** were destroyed by passing oxygen through their solutions. Thus from the chemical evidence no indication could be obtained as to the fate of the lost carbon atom.

Product identification

The IR and NMR data of the new complexes **4**, **5**, and **6** are given in Table 1. With reference to the fully characterized complex **3a** [8,10] these allowed the quick identification of **4a**, **4b**, and **4c**. The composition of **6** was obtained from an EI mass spectrum, and the similarity of **5** and **6** is obvious from the spectra. Both **5** and **6** represent a new product type in the very well investigated field of alkylidyne bridged trimetal clusters where almost all MCo_2 combinations except for these have been published before.

In order to confirm the new structure type a structure determination was made for **6**. Its pertinent results are given in Table 2 and Fig. 1. The molecules of **6** are of

Table 1

IR and NMR data of new complexes

No.	$\nu(CO)$ [a]	δ [b]	
4a	2084w 2045vs 2040vs 2019m 1994m 1980w	7.35 (Ph)	5.46 (Cp)
4b	2075w 2041vs 2031vs 2008s 1990w 1975w	5.48 (Cp)	1.33 (t-Bu)
4c	2075m 2036vs 2008vs 1990s 1975sh 1950sh	5.49 (Cp)	2.68 (Me)
5	2082s 2040vs 2032vs 1992w 1984w 1919w	7.54 (Ph)	4.43 (Cp)
6	2080s 2036vs 2030vs 1988w 1952w	7.40 (Ph)	4.82 (Cp)

[a] C_6H_{12}, cm^{-1}. [b] $CDCl_3$, int. TMS.

Table 2

Important bond lengths and angles for **6**

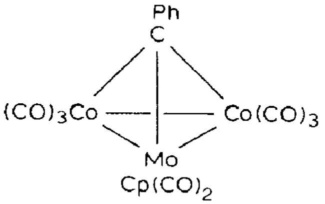
Distances (pm)		Angles (degs)	
Ru-Co1	265.5(1)	Co1-Ru-Co2	57.3(1)
Ru-Co2	257.3(1)	Ru-Co1-Co2	59.7(1)
Co1-Co2	250.6(1)	Ru-Co2-Co1	63.0(1)
Ru-C1	206.2(4)	Ru-C1-Co1	84.5(2)
Co1-C1	188.2(4)	Ru-C1-Co2	81.2(2)
Co2-C1	188.7(4)	Co1-C1-Co2	83.4(2)
Ru-C11	187.3(4)	Ru-C1-C2	126.3(3)
Ru-C(Cp)	223.3(av)	Co1-C1-C2	132.0(3)
Co-C(CO)	178.8(av)	Co2-C1-C2	131.7(3)
C1-C2	149.2(5)		

Table 3

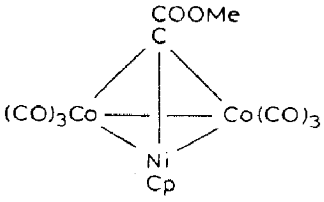
Bond distance comparison (pm) for **6**, **7**, and **8**

	7 M = Mo	**6** M = Ru	**8** M = Ni
Co–Co	248.3	250.6	247.1
M–Co(av)	267.7	261.4	238.0
Co–C_{ap}(av)	193	188.5	188
M–C_{ap}	210	206.2	183

the usual CM_3 tetrahedrane type, the μ_3-CPh unit being the leftover-part of the original C≡CPh ligand. Contrary to expectation, the structure of **6** cannot be idealized as having mirror symmetry: the Ru–Co bond lengths are noticeably different, and the Ru–Co2 bond is spanned by a semi-bridging CO ligand (C33–O33). Otherwise the molecular features are normal: the M–M and M–C_{ap} bonds are of the usual length, and the C1–C2 vector is normal to the $RuCo_2$ plane (89.1°). The structure determination of **6** completes a series of similar structures for clusters $(\mu_3\text{-RC})Co_2(CO)_6ML_n$, with ML_n being $MoCp(CO)_2$ for **7**, RuCp(CO) for **6**, and NiCp for **8**.



(**7** [11])



(**8** [12])

As Table 3 shows and as we have demonstrated for similar (μ_3-RP)-bridged clusters before [13] the differences between these three clusters can be found in the M–Co and M–C_{ap} bond lengths, while the Co–Co and Co–C_{ap} bond lengths vary very little. This can be traced back to the radius of the metal atoms, becoming smaller in the series Mo > Ru > Ni. But to our opinion [13] ligand crowding plays an equally important role, being pronounced in **7**, noticeable in **6** (see bending of CO groups away from the Cp ligand), and absent in **8**. Thus the "soft" metal–metal bonds, except maybe in **8**, are stretched to more than normal lengths in these clusters.

Mechanistic considerations

The oxidative decarbonation of **3** and **4a** was sufficiently unusual to warrant a detailed investigation. This was performed by introducing ^{13}C at the α position of the acetylide **2a** according to the following sequence of standard organic reactions:

$$^{13}CH_3I \rightarrow \left[Ph_3P^{13}CH_3\right]^+ I^- \rightarrow PhCH{=}^{13}CH_2 \rightarrow PhCHBr{-}^{13}CH_2Br \rightarrow$$

$$PhC{\equiv}^{13}CH \rightarrow Cp(CO)_2Ru{-}^{13}C{\equiv}CPh$$

It was then ascertained by mass spectrometry that the cluster **4a** formed from ^{13}C

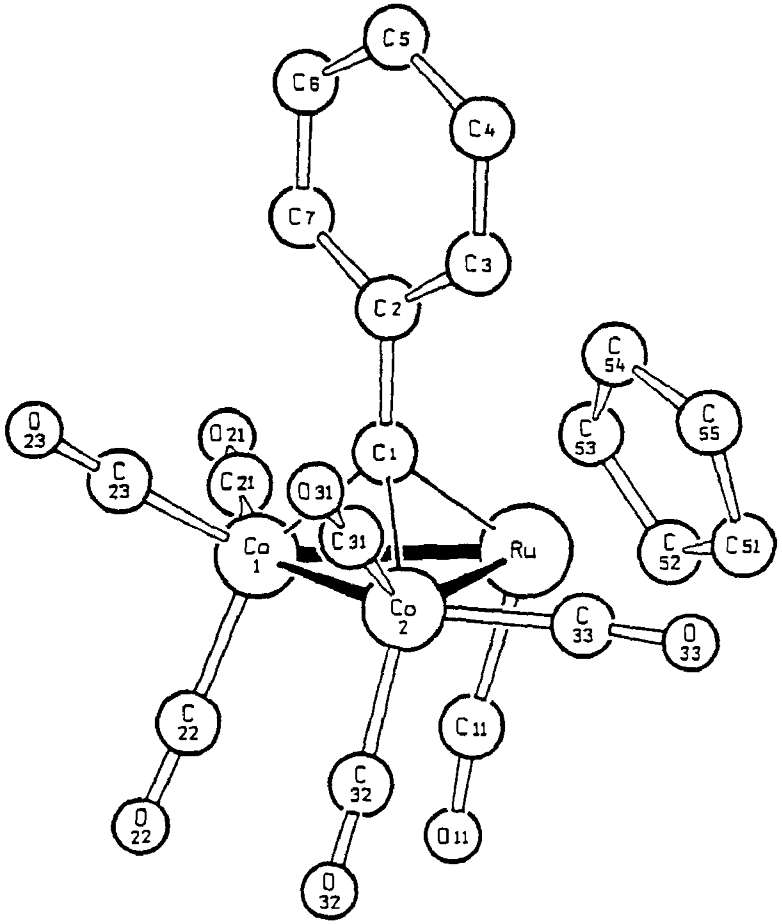


Fig. 1. Molecular structure of $RuCo_2(CO)_7Cp(\mu_3\text{-}CPh)$ (6).

labelled **2a** and $Co_2(CO)_8$ contained one non-carbonyl C atom which was 90% ^{13}C according to the isotopic purity of the $^{13}CH_3I$ starting material. After the oxidative decarbonation of the ^{13}C labelled **4a**, mass spectrometry provided the surprising result that most of the ^{13}C was still in the isolated product **6**, but now all in the form of CO ligands. Figure 2 shows this by giving the isotopic patterns for the EI-MS peaks for the parent cluster **6** and its seven CO elimination products. It is immediately obvious that the acetylide α-C atom is oxidized to a CO unit. That this is the case quantitatively can be derived from the quantitative interpretation of Fig. 2. Taking into account eight CO ligands in **4a** plus one CO precursor (^{13}C) gives nine possible CO's before the formation of **6** which itself has seven CO's. If all nine possible CO's of **4a** have the same chance of ending up in **6** and if one of them is 90% ^{13}C, the molecule of **6** should contain $0.9 \times 7/9$ of one ^{13}C labelled CO ligand. The white bars in Fig. 2 represent the isotopic composition based on this assumption. Successive CO elimination from the molecular ion of **6** should then systematically reduce the artificial ^{13}C content until it reaches zero for the CO-free cluster ion. Checking this and other possibilities by calculating the isotopic compositions for all CO containing fragments (including the natural ^{13}C abundance) gave the highest agreement with the observed isotopic pattern for the assumption made

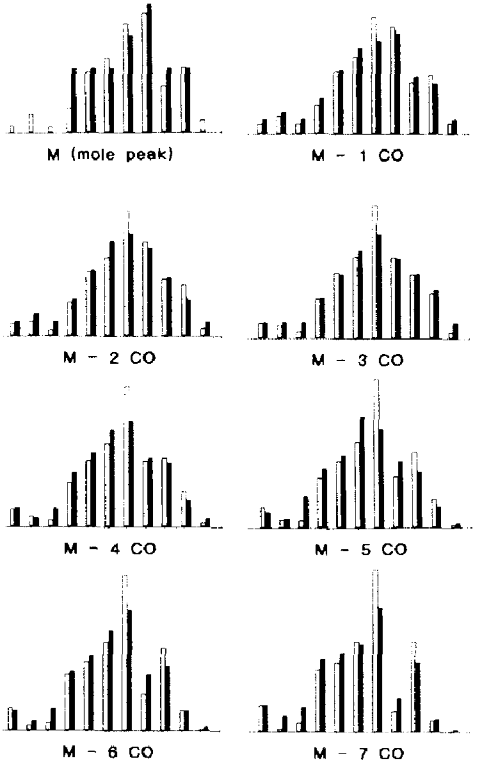


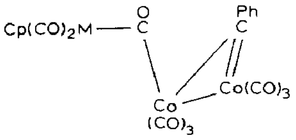
Fig. 2. Calculated (white bars) and observed (black bars) isotopic patterns for the parent ion and the seven CO-elimination products of cluster **6**.

above. This means that the acetylenic α-C atom is attacked by oxygen and converted very early in the reaction sequence to a CO unit which behaves exactly like the eight other CO ligands, i.e. having a 2/9 chance of being eliminated and a 7/9 chance of ending up as a CO ligand in **6**.

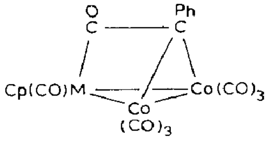
Discussion

To our knowledge, the **4a** → **6** interconversion is the first one where oxidation has transformed part of an alkyne into a CO ligand. The most similar case of precedence is the hydrolytic transformation of $[H_2Os_3(CO)_9(\mu_3\text{-}C{\equiv}CH)]^+$ to $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ and CO [14], and a related oxidation of a vinylidene ligand to CO in the complex $[Ru(C{=}CHR)(PPh_3)_2Cp]^+$ has been mentioned [15]. Previous investigations have focused more on the cleavage of CO ligands, like in the formation of $HFe_4(CO)_{12}(\mu_4\text{-}CH)$ from $Fe_4(CO)_{13}^{2-}$ [16] or in the formation of $CpWOs_3(CO)_9(\mu_3\text{-}C\text{–}CH_2Tol)(\mu_2\text{-}O)$ from $CpWOs_3(CO)_{11}(\mu_3\text{-}CO\text{–}CH_2Tol)$ [17]. And there have been many approaches to the reductive cleavage of CO related to work on the cluster-surface analogy or on a coal-based organic chemistry. The oxidative decarbonation observed here demonstrates the principle of microscopic reversibility for this part of C–O chemistry in providing a new way of CO formation.

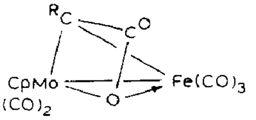
As to the detailed mechanism of the oxidative decarbonation several possibilities may be envisaged. Assuming initial attack of oxygen at the acetylide α carbon atom and adhering to the 18-electron rule two types of primary reaction intermediates come into mind. Of these, **9** would result from $C\equiv C$ scission followed by oxidation, and **10** would represent initial oxidation and loss of one CO ligand. In both cases the emergence of the μ_3-CPh ligand can be visualized. But both must be short-lived intermediates since both represent hitherto unobserved bonding types: the CO bridge without a metal bond in **9**, and the μ_3-bridging ketenyl ligand in **10**. Some resemblance to the latter is, however, found in **11** which also results from an oxydation with O_2 [18].



(9)



(10)



(11)

The unusual formation of **5** and **6** has provided the first convenient synthetic procedure for mixed metal clusters of the (μ_3-RC)M_3 type containing Cp(CO)Fe and Cp(CO)Ru building blocks. Previously only the Fe containing system could be obtained inconveniently and in small yields [19]. Including **5** and **6**, we have now modified the basic (RC)$Co_3(CO)_9$ cluster such that it contains Cr, Mo, W, Fe, Ru, Os, Rh, and Ni in place of Co [20]. The potential of **5** or **6** to be precursors of chiral clusters with three different metal atoms has also been tested successfully [21]. Further investigations of **5** and **6** will focus on their ability to undergo reactions in the ligand sphere utilizing the μ_3-CPh unit as an organic building block, a reaction type for which the **7**-type clusters are sterically too crowded and the **8**-type clusters are too labile.

Experimental part

The experimental techniques and the spectroscopic instrumentation were as previously described [22]. The starting materials were prepared according to the given references. The ^{13}C labelled phenyl acetylene was prepared according to the sequence in the text by standard Organic Synthesis procedures. Table 4 gives the analytical characterization of the new compounds.

4a: 1.001 g (3.10 mmol) **2a** in 20 ml of benzene were dropped within an hour at room temperature into 1.380 g (4.04 mmol) of $Co_2(CO)_8$ in 20 ml of benzene with stirring. The solvent was removed in vacuo and the residue chromatographed with hexane/CH_2Cl_2 (10/1) over a 2 × 35 cm silica gel column: first fraction (red-brown): small amounts of $Co_2(CO)_8$; second fraction (brown): small amounts of $Co_4(CO)_{12}$; third fraction (orange): small amounts of an unidentified compound; fourth fraction (green): after reducing the volume and crystallization at $-30\,°C$, 1.493 g (79%) of black, crystalline **4a** remained.

4b: Like **4a** from 274 mg (1.05 mmol) **2b** and 383 mg (1.11 mmol) $Co_2(CO)_8$. Yield: 306 mg (53%) of black, crystalline **4b**.

4c: Like **4a** from 382 mg (1.26 mmol) **2c** and 413 mg (1.20 mmol) $Co_2(CO)_8$. Yield: 330 mg (47%) of black, crystalline **4c**.

6: Through a solution of 640 mg (1.05 mmol) of **4a** in 20 ml of hexane and 10 ml of CH_2Cl_2 was passed a slow stream of pure oxygen five times for one minute during

Table 4. Characterization of the new complexes

No.	M.p. [°C]	Formula (mol.wt.)	Analysis (calcd. (found) (%))		
			C	H	Co
4a	130	$C_{21}H_{10}Co_2O_8Ru$	41.40	1.65	19.35
		(609.2)	41.18	1.60	19.81
4b	110	$C_{16}H_8Co_2O_8Ru$	35.12	1.47	21.54
		(547.2)	34.94	1.40	21.32
4c	94	$C_{19}H_{14}Co_2O_8Ru$	38.73	2.39	20.00
		(589.3)	38.66	2.59	19.74
5	154	$C_{19}H_{10}Co_2FeO_7$	43.55	1.92	22.49
		(524.0)	43.53	1.91	22.26
6	152	$C_{19}H_{10}Co_2O_7Ru$	40.09	1.77	20.71
		(569.2)	40.14	1.89	20.28

Table 5. Atomic parameters for **6**

Atom	x	y	z	U
Ru	0.2319(0)	0.8357(0)	0.0729(0)	0.0439(2)
Co1	0.0726(1)	0.8391(1)	0.1892(0)	0.0435(3)
Co2	0.1663(1)	0.6658(1)	0.1450(0)	0.0496(3)
C1	0.2579(4)	0.7887(4)	0.1922(2)	0.040(2)
C3	0.5027(4)	0.7348(3)	0.2504(2)	0.070(3)
C4	0.6247(4)	0.7474(3)	0.3065(2)	0.100(5)
C5	0.6318(4)	0.8274(3)	0.3650(2)	0.109(5)
C6	0.5169(4)	0.8947(3)	0.3673(2)	0.094(5)
C7	0.3948(4)	0.8821(3)	0.3112(2)	0.065(3)
C2	0.3877(4)	0.8021(3)	0.2528(2)	0.048(2)
H3	0.4978(4)	0.6797(3)	0.2102(2)	0.08(2)
H4	0.7038(4)	0.7010(3)	0.3049(2)	0.11(2)
H5	0.7158(4)	0.8360(3)	0.4036(2)	0.15(3)
H6	0.5213(4)	0.9498(3)	0.4075(2)	0.18(4)
H7	0.3157(4)	0.9285(3)	0.3128(2)	0.09(2)
C51	0.3557(5)	0.8552(3)	−0.0275(3)	0.076(4)
C52	0.2756(5)	0.9496(3)	−0.0226(3)	0.071(4)
C53	0.3216(5)	0.9979(3)	0.0536(3)	0.079(4)
C54	0.4302(5)	0.9333(3)	0.0958(3)	0.092(5)
C55	0.4512(5)	0.8451(3)	0.0457(3)	0.086(4)
H51	0.3468(5)	0.8068(3)	−0.0723(3)	0.42(8)
H52	0.2031(5)	0.9762(3)	−0.0636(3)	0.16(3)
H53	0.2857(5)	1.0627(3)	0.0731(3)	0.13(3)
H54	0.4805(5)	0.9468(3)	0.1489(3)	0.23(5)
H55	0.5182(5)	0.7886(3)	0.0590(3)	0.13(3)
C11	0.0457(5)	0.8199(5)	0.0214(3)	0.054(3)
O11	−0.0626(4)	0.8136(4)	−0.0178(2)	0.081(3)
C21	0.0795(6)	0.9820(5)	0.1913(3)	0.064(3)
O21	0.0858(6)	1.0717(4)	0.1952(3)	0.103(4)
C22	−0.1099(5)	0.8091(5)	0.1521(3)	0.064(3)
O22	−0.2249(4)	0.7886(5)	0.1321(3)	0.102(3)
C23	0.0726(6)	0.8084(5)	0.2927(3)	0.064(3)
O23	0.0761(6)	0.7905(5)	0.3584(2)	0.110(4)
C31	0.2318(6)	0.5775(4)	0.2243(3)	0.058(3)
O31	0.2729(5)	0.5216(4)	0.2757(3)	0.089(3)
C32	0.0034(7)	0.5999(5)	0.1023(4)	0.082(4)
O32	−0.0977(6)	0.5570(5)	0.0797(4)	0.147(5)
C33	0.2618(7)	0.6427(5)	0.0640(3)	0.070(3)
O33	0.3223(6)	0.5994(4)	0.0191(3)	0.093(3)

an 8 hour period at room temperature. After filtration, concentration in vacuo and crystallization at −30 °C 259 mg (44%) of black, crystalline **6** remained.
5: Over a solution of 194 mg (0.34 mmol) of **3a** was passed a slow stream of pure oxygen for 3 h at 40 °C. The solvent was removed in vacuo and the residue dissolved in hexane, filtered and chromatographed with hexane over a 2 × 30 cm silica gel column. After a small unidentified brown fraction, a purple fraction, after recrystallization from hexane at −30 °C yielded 36 mg (20%) of black, crystalline **5**.

Structure determination [23]*

Crystals of **6** (0.60 × 0.25 × 0.15 mm) were obtained from n-hexane: space group $P2_1/c$, a 960.3 (1), b 1253.3(2), c 1674.7(3) pm, β 98.77(1)°, $Z =$ d, $d_{\text{calcd.}}$ 1.90, $d_{\text{obsd.}}$ 1.89 g cm^{-3}, μ 24.8 cm^{-1}, 3282 reflexions with $I \geq 3\sigma(I)$, 252 variables, $R = 0.036$, residual electron density maxima +1.3 and -1.2×10^6 e pm^{-3}.

The data set was obtained with Ag-K_α radiation on a Nonius CAD4 diffractometer and the structure solved without absorption correction by direct methods using the programs SHELX [24] and SCHAKAL for plotting [25]. Table 5 lists the atomic parameters.

Acknowledgment

This work was supported by the Fonds der Chemischen Industrie and by the Rechenzentrum der Universität Freiburg. Helpful discussions with Prof. J.R. Shapley, Illinois, in the context of a NATO supported collaboration, are gratefully acknowledged.

References and Notes

1 cf. 100 Years of Metal Carbonyls; Proceedings of the Fourth European symposium on Inorganic Chemistry, Freiburg 1988. Special Issue of J. Organomet. Chem., 372 (1989) No. 1.
2 V.J. Johnston, F.W.B. Einstein, and R. Pomeroy, Organometallics, 7 (1988) 1867.
3 E. Roland and H. Vahrenkamp, Chem. Ber., 118 (1985) 1133.
4 E.W. Abel and F.G.A. Stone, Quart. Rev. Chem. Soc. (London), 24 (1970) 498.
5 cf. W.A. Herrmann, Angew. Chem., 100 (1988), 1269; Angew. Chem. Int. Ed. Engl., 27 (1988) 1297.
6 E. Roland, W. Bernhardt, and H. Vahrenkamp, Chem. Ber., 119 (1986) 2566; W. Bernhardt and H. Vahrenkamp, J. Organomet. Chem., 355 (1988) 427.
7 W. Bernhardt and H. Vahrenkamp, Organometallics, 5 (1986) 2388.
8 K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Jpn., 45 (1972) 2664; K. Yasufuku, K. Aoki, and H. Yamazaki, Bull. Chem. Soc. Jpn., 48 (1975) 1616.
9 M.I. Bruce, M.G. Humphrey, J.G. Matisons, S.K. Roy, and A.G. Swincer, Aust. J. Chem., 37 (1984) 1955.
10 M.I. Bruce, D.N. Duffy, and M.G. Humphrey, Aust. J. Chem., 39 (1986) 159.
11 H. Beurich and H. Vahrenkamp, Chem. Ber., 115 (1982) 2385.
12 R. Blumhofer, K. Fischer, and H. Vahrenkamp, Chem. Ber., 119 (1986) 194.
13 M. Müller and H. Vahrenkamp, Chem. Ber., 116 (1983) 2765.
14 E. Boyar, A.J. Deeming, and S.E. Kabir, J. Chem. Soc. Chem. Commun., (1986) 577.
15 M.I. Bruce, A.G. Swincer, and R.C. Wallis, J. Organomet. Chem., 171 (1979) C5.
16 K.H. Whitmire and D.F. Shriver, J. Am. Chem. Soc., 103 (1981) 6754.
17 J.R. Shapley, J.T. Park, M.R. Churchill, J.W. Ziller, and C.R. Beenan, J. Am. Chem. Soc., 106 (1984) 1144.

---

* Reference numbers with asterisks indicate notes in the list of references.

18 M.E. Garcia, J.C. Jeffery, P. Sherwood, and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1986) 802.

19 H. Beurich, R. Blumhofer, and H. Vahrenkamp, Chem. Ber., 115 (1982) 2409; S. Jensen, B.H. Robinson, and J. Simpson, J. Chem. Soc. Chem. Commun., (1983) 1081.

20 H. Vahrenkamp, Comm. Inorg. Chem., 4 (1985) 253.

21 W. Bernhardt and H. Vahrenkamp, unpublished.

22 W. Deck, M. Schwarz, and H. Vahrenkamp, Chem. Ber., 120 (1987) 1515.

23 Further details of the structure determination are available from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, upon citation of the depository no. CSD 53627, the authors and reference to this paper.

24 G.M. Sheldrick, Universität Göttingen, Germany.

25 E. Keller, Universität Freiburg, Germany.