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BIMETALLIC BIPHENYLENE BISCARBENE COMPLEXES: SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND REACTIVITY TOWARDS SOME NUCLEOPHILIC REAGENTS

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Summary

The reaction of *p*-biphenylenedilithium with hexacarbonyl-chromium or -tungsten and subsequent alkylation by triethyloxonium tetrafluoroborate yields the μ-[*p*-biphenylenebis[(ethoxy)carbene]]bis(pentacarbonylmetal) complexes: $(CO)_5M{=}C(OEt)$-*p*,*p'*-$(C_6H_4)_2C(OEt){=}M(CO)_5$ ($M = Cr$ (**1**), $M = W$ (**2**)). An X-ray diffraction study of **1** has shown that the molecule is centrosymmetric; that there is practically no delocalization between the two subunits of the biphenyl ligand, and that both rings are strictly coplanar. Aminolysis and insertion of ynamine into the metal–carbon bond give new bis(aminocarbene) complexes.

We have recently described the synthesis of some bimetallic bis-carbene complexes by addition of dianionic systems to hexacarbonylmetals and alkylation of the bisacylmetallates with $[Et_3O][BF_4]$ [1]. In an exploration of the generality of this method, we have now examined the reactions of some bimetallated biphenyl derivatives with hexacarbonyl-chromium and -tungsten.

Results

(1) Synthesis

p-Biphenylenedilithium [2] reacts with $Cr(CO)_6$ and $W(CO)_6$ to give bisacylmetallate complexes, which are alkylated by $[Et_3O][BF_4]$ to give new bimetallic biscarbene compounds: $(CO)_5M{=}C(OEt)$-*p*,*p'*-$(C_6H_4)_2(OEt)C{=}M(CO)_5$ ($M = Cr$ (**1**), $M = W$ (**2**)) (Scheme 1). The reactions of the hexacarbonyls with *o*-biphenylenedilithium [3] do not give the *o*-biphenylenebis-carbene complexes (the latter would

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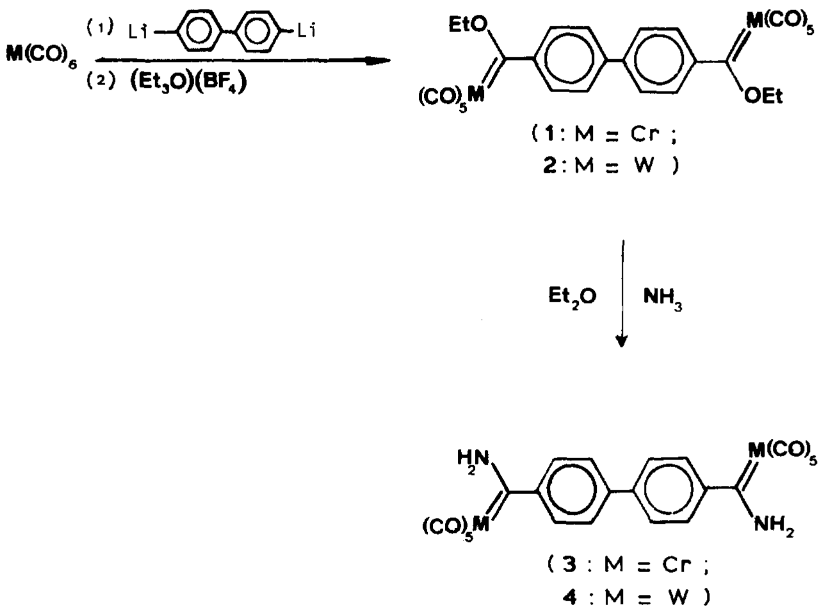


SCHEME 1

be chiral species owing to the presence of bulky substituents in the *o*-positions), the mono-carbene complex o-$C_6H_5C_6H_4C(OEt){=}Cr(CO)_5$ being isolated [4].

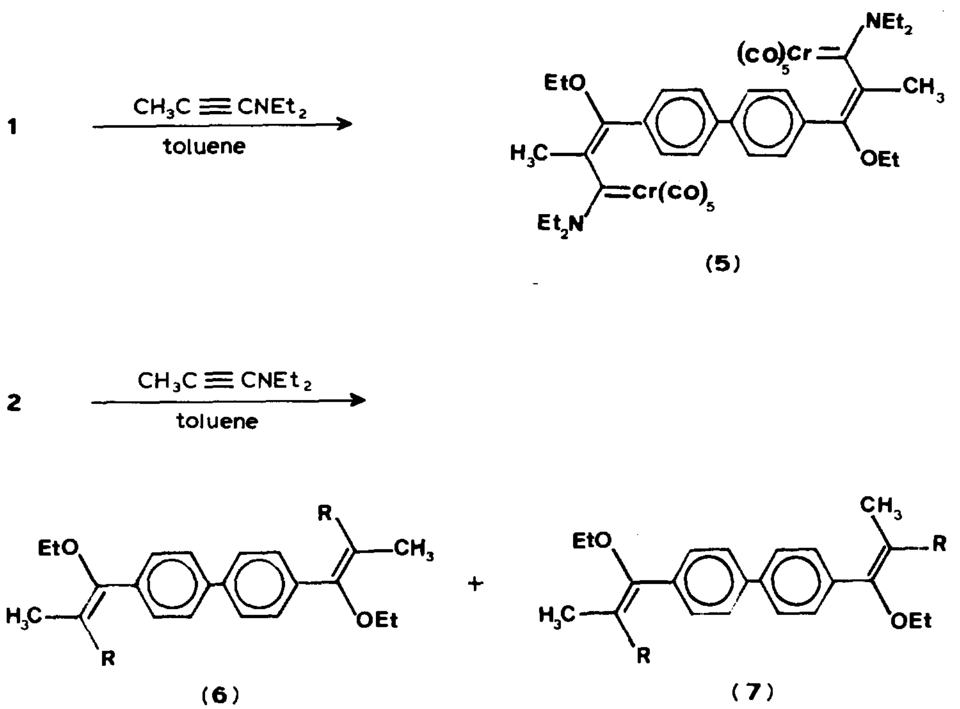
(2) Reactions towards nucleophilic reagents

These reactions are useful for studies of carbene functions, which are highly susceptible to nucleophilic attack [5].

(a) With NH_3. Compounds **1** and **2** react in Et_2O with ammonia to give bis(aminocarbene) complexes **3** and **4**, by substitution of ethoxy groups by amino groups. The products can be purified by chromatography on silica gel. Similar behaviour has been described previously for mono- and chelating bis-carbene complexes [6,7].

(b) With 1-diethylamino-1-propyne $CH_3C{\equiv}CNEt_2$. For monocarbene complexes this reaction involves insertion of the alkyne into the metal–carbene bond and provides a route to aminovinylcarbene compounds with a longer side-chain [8]. In the case of a chelating bis-carbene complex, *cis*-tetracarbonylbis(1,2-diphenyl-1,2-ethanediyldiethoxy)carbenetungsten, we found that a metallocyclic carbenevinyl complex was formed via insertion of an alkyne unit into a carbene–oxygen bond [9].

For compounds **1** and **2**, both carbene functions are equivalent, and an alkyne unit inserts into each of the two carbene–metal bonds. The reaction is stereoselective for the compound **1** (M = Cr), the aminocarbene **5** with both alkenylcarbene ligands in the *E*-configuration being isolated. From compound **2** (M = W), two isomers were isolated: complex **6**, with the two vinyl ligands in the same *E*-configuration, and complex **7**, with one chain in the *E*- and the other in the *Z*-configuration (**6**/**7** = 25/1) (Scheme 2).



SCHEME 2. R = $C(NEt_2)=W(CO)_5$; 6/7 = 25/1.

Spectroscopic data

(1) IR spectra (Table 1)

The shape and the intensity of the $\nu(CO)$ absorption bonds of the compounds **1**–**7** are characteristic of carbene complexes with a pentacarbonyl structure. In complexes **3**–**6**, these bands are shifted to lower frequencies, in accord with the good σ-donor/weak π-acceptor ratio for the amino carbene ligands [10].

(2) ^1H NMR spectra (Table 2)

The NH_2 protons of the compounds **3** and **4** appear at low field as two distinct multiplets, this is consistent with the double bond character of the $C_{carbene}=N$ bond.

TABLE 1

$\nu(CO)$-ABSORPTION FREQUENCIES (cm^{-1}) FOR COMPOUNDS 1–7 (Perkin–Elmer 357)

Compound		Solvent
1	2070(m), 1945(vs)	CH_2Cl_2
2	2070(m), 1945(vs)	CH_2Cl_2
3	2060(m), 1935(vs)	CH_2Cl_2
4	2060(m), 1935(vs)	CH_2Cl_2
5	2055(m), 1970(w), 1935(vs), 1920(s)	pentane
6	2060(m), 1970(w), 1935(vs), 1920(s)	pentane
7	2060(m), 1970(w), 1935(vs), 1920(s)	pentane

TABLE 2

^1H NMR SPECTRA (Bruker WP 200) δ(ppm)

Compounds	Solvent	H_2N	C_6H_4	OCH_2,NCH_2	$=\!\!/\,CH_3$	OCH_2CH_3,	NCH_2CH_3
1	$CDCl_3$		7.70	5.06		1.72	
			(d,4H)	(q,4H)		(t,6H)	
			7.45				
			(d,4H)				
2	CD_3COCD_3		7.94	5.34		1.90	
			(d,4H)	(q.4H)		(t,6H)	
			8.07				
			(d,4H)				
3	CD_3COCD_3	10.89	7.89				
		(m,2H)*Z*	(d,4H)				
		10.25	7.46				
		(m,2H)*E*	(d,4H)				
4	CD_3COCD_3	10.81	7.78				
		(m,2H)*Z*	(d,4H)				
		10.58	7.58				
		(m,2H)*E*	(d,4H)				
5	$CDCl_3$		7.50	3.2–4.5		2	1–1.6
			(d,4H)	(m,12H)		(s,6H),	(m,18H)
			7.26				
			(d,4H)				
			7.49	3.2–4.3		1.91	1–1.5
			(d,4H)	(m,12H)		(s,6H),	(m,18H)
6	$CDCl_3$		7.25				
			(d,4H)				
7	$CDCl_3$		7.69–7.28	3.26–4.23	1.91(*E*)		0.93–1.5
					(s,3H)		
			(m,8H)	(m,12H)	1.67(*Z*)		(m,18H)
					(s,3H)		

The *E*,*E* or *E*,*Z* configurations of the alkenyl chains can be readily distinguished by the chemical shift of the vinylic methyl group. In **5** and **6**, both CH_3 groups are equivalent. In **7**, the signal from the methyl of the *Z*-alkenyl chain is at higher field ($\Delta\delta$ 0.24 ppm) than that from the CH_3 of the chain with the *E*-configuration. This can be attributed to the non-coplanarity of the *Z*-methyl group and the phenyl ring [11].

(3) ^{13}C NMR spectra (Table 3)

The signals from the carbene carbons in ethoxy compounds **1**, **2** are at lower fields than those from amino compounds **3–6** ($\Delta\delta$ 60 ppm).

(4) X-Ray diffraction study of complex 1 (Figure 1)

It was of interest to ascertain whether there is delocalization of the π-electrons involving the whole intermetal framework in these biphenyl derivatives, and so a single crystal study of compound **1** was undertaken.

(a) Results. The structure of compound **1** was solved by direct methods. Refinement was carried out by full matrix least squares for all non-hydrogen atomic coordinates and anisotropic thermal parameters. A Fourier difference map than

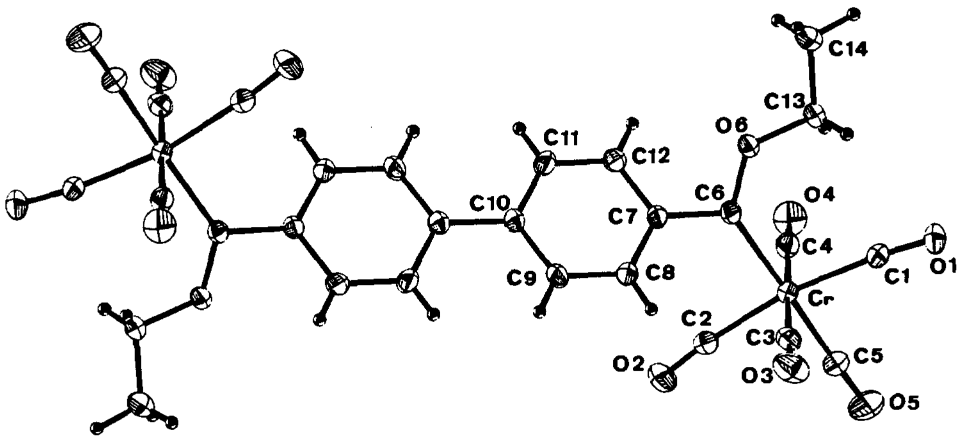


Fig. 1. Structure of complex 1.

showed all hydrogen atoms. Their atomic coordinates were refined using isotropic thermal parameters fixed at $U = 0.05$. The final reliability factors are $R = 0.026$ and $R_w = 0.028$ with: $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_w = (\Sigma w(| F_o | - | F_c |)^2 / \Sigma w F_o^2)^{1/2}$.

The highest ratio shift/e.s.d. of the last refinement cycle was found to be 1.0 for three parameters only. The main bond distances and bond angles are shown in Table 4. The atomic coordinates are listed in Table 5. All calculations were performed on a DEC-VAX 725 using Crystals programs. Lists of thermal parameters and structure factors are available from the authors.

(b) Discussion. With one molecule per unit cell and with a centrosymmetric unit cell, the molecule is centrosymmetric. In contrast to the usual situation for diphenyl derivatives, the two rings are strictly coplanar since they correspond to each other through the inversion center.

Substituted diphenyl is known to have a dihedral angle between phenyl rings. This is due to steric hindrance. For instance, the angle determined by electron diffraction in gaseous state is 60° for 2,2-difluorodiphenyl [12]. This angle was also measured by electron diffraction in gaseous state on diphenyl itself and was found to be 45° [13]. Later the problem was addressed again in the solid state by X-ray diffraction. Almost simultaneously three studies [14–16] were described, and all of them revealed a planar centrosymmetric molecule. (The question of pseudocentrosymmetry was thoroughly discussed by Trotter [14] and ruled out.) The reported inter-ring C–C distance, 1.506(17) Å [16], 1.497(21) Å [15], or 1.507(32) Å [14] suggests that π delocalization does not extend over both phenyl rings.

More recently, the structure was refined at 293 and 100 K using the Cruickshank rigid body model by Charbonneau and Delugeard [17]. This revealed a high value for the libration component lying along the longest axis of the molecule; the root mean square angle is 10.4° (1) at 293 K and 6.8° (2) at 110 K. It was inferred that the molecule becomes non planar in the liquid state and in the gaseous state.

As already stated the title compound is exactly planar. The largest deviation of a phenyl carbon from the mean phenyl plane is 0.020(6) Å. The inter-ring C–C distance is equal to 1.485(4) Å. It thus seems that any π delocalization from one

(Continued on p. 218)

TABLE 3

^{13}C NMR SPECTRA (Bruker WP 200) δ(ppm)

Compound (Solvent)	$C_{carbene}$	CO_{trans}	CO_{cis}	$=C{\diagup}^{OEt}$	$=C{\diagup}^{CH_3}$	$C_{aromatic}$	OEt		NEt_2		CH_3
							CH_2	CH_3	CH_2	CH_3	
1	347.7	224.3	216.4			153.0; 141.6	77.3	15.3			
($CDCl_3$)						126.9; 124.2					
2	318.1	203.5	197.4			154.7; 142.9					
($CDCl_3$)						127.5; 126.8	80.3	15.1			
3	282.61	224.84	218.76			153.3; 141.13					
(CD_3COCD_3)						127.66; 124.11					
4	259.67	206.29	204.75			153.4; 141.69					
(CD_3COCD_3)						127.69; 125.5					
5	271	223.04	216.69	139.72	137.9	134.23; 133.85	65.86		52.85 (*Z*)	13.73 (*Z*)	
($CDCl_3$)						127.79; 126.68		15.53	48.51 (*E*)	13.34 (*E*)	16.74
6	253.03	202.71	197.94	139.69	138.69	134.63; 133.72	66.16		55.15 (*Z*)	13.66 (*Z*)	
($CDCl_3$)						127.96; 126.74		15.54	47.05 (*E*)	13.16 (*E*)	16.62

TABLE 4

BOND LENGTHS (Å) AND BOND ANGLES (°) OF COMPOUND 1

Cr(1)–C(1)	1.887(3)	C(2)–Cr(1)–C(1)	170.0(1)
Cr(1)–C(2)	1.912(4)	C(3)–Cr(1)–C(1)	88.5(1)
Cr(1)–C(3)	1.902(4)	C(3)–Cr(1)–C(2)	90.2(1)
Cr(1)–C(4)	1.896(4)	C(4)–Cr(1)–C(1)	90.5(1)
Cr(1)–C(5)	1.865(4)	C(4)–Cr(1)–C(2)	90.8(1)
Cr(1)–C(6)	2.051(4)	C(4)–Cr(1)–C(3)	178.9(2)
C(1)–O(1)	1.140(4)	C(5)–Cr(1)–C(1)	84.7(2)
C(2)–O(2)	1.131(4)	C(5)–Cr(1)–C(2)	85.4(2)
C(3)–O(3)	1.133(4)	C(5)–Cr(1)–C(3)	91.5(2)
C(4)–O(4)	1.137(4)	C(5)–Cr(1)–C(4)	88.2(2)
C(5)–O(5)	1.137(4)	C(6)–Cr(1)–C(1)	97.7(2)
C(6)–O(6)	1.321(3)	C(6)–Cr(1)–C(2)	92.3(2)
C(6)–C(7)	1.485(4)	C(6)–Cr(1)–C(3)	91.6(2)
O(6)–C(13)	1.446(4)	C(6)–Cr(1)–C(4)	88.7(2)
C(7)–C(8)	1.376(4)	C(6)–Cr(1)–C(5)	176.1(2)
C(7)–C(12)	1.394(4)	O(1)–C(1)–Cr(1)	172.9(3)
C(8)–C(9)	1.376(4)	O(2)–C(2)–Cr(1)	173.3(3)
C(9)–C(10)	1.390(4)	O(3)–C(3)–Cr(1)	178.1(4)
C(10)–C(10)	1.485(5)	O(4)–C(4)–Cr(1)	177.1(3)
C(10)–C(11)	1.379(4)	O(5)–C(5)–Cr(1)	177.1(4)
C(11)–C(12)	1.370(4)	C(7)–C(6)–O(6)	105.1(2)
C(13)–C(14)	1.486(5)	Cr(1)–C(6)–O(6)	129.4(3)
C(8)–H(8)	0.86(3)	Cr(1)–C(6)–C(7)	125.2(3)
C(9)–H(9)	0.90(3)	C(13)–O(6)–C(6)	124.7(2)
C(11)–H(11)	0.86(3)	C(8)–C(7)–C(6)	123.8(3)
C(12)–H(12)	0.89(3)	C(12)–C(7)–C(6)	119.3(3)
C(13)–H(111)	0.92(3)	C(12)–C(7)–C(8)	36.9(3)
C(13)–H(132)	1.01(3)	C(9)–C(8)–C(7)	121.7(3)
C(14)–H(141)	0.98(3)	H(8)–C(8)–C(7)	120.7(21)
C(14)–H(142)	0.92(3)	H(8)–C(8)–C(9)	117.6(22)
C(14)–H(143)	0.94(3)	C(10)–C(9)–C(8)	121.8(3)
		H(9)–C(9)–C(8)	119.8(20)
		H(9)–C(9)–C(10)	118.2(20)
		C(10)–C(10)–C(9)	122.3(3)
		C(11)–C(10)–C(9)	115.9(3)
		C(11)–C(10)–C(10)	121.7(3)
		C(12)–C(11)–C(10)	122.8(3)
		H(11)–C(11)–C(10)	117.6(22)
		H(11)–C(11)–C(12)	119.5(22)
		C(11)–C(12)–C(7)	120.8(3)
		H(12)–C(12)–C(7)	118.9(20)
		H(12)–C(12)–C(11)	119.9(20)
		C(14)–C(13)–O(6)	106.9(3)
		H(131)–C(13)–O(6)	104.7(20)
		H(131)–C(13)–C(14)	111.5(20)
		H(132)–C(13)–O(6)	108.8(18)
		H(132)–C(13)–C(14)	112.8(18)
		H(132)–C(13)–H(131)	111.7(27)
		H(141)–C(14)–C(13)	111.0(19)
		H(142)–C(14)–C(13)	108.9(21)
		H(142)–C(14)–H(141)	105.5(29)
		H(143)–C(14)–C(13)	111.4(21)
		H(143)–C(14)–H(141)	107.1(27)
		H(143)–C(14)–H(142)	112.7(30)

TABLE 5

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.87156(8)	−0.25999(6)	−0.26630(5)	0.0396
C(1)	1.1013(5)	−0.1902(4)	−0.3190(3)	0.0462
O(1)	1.2505(4)	−0.1628(3)	−0.3529(2)	0.0605
C(2)	0.6730(5)	−0.3655(4)	−0.2150(3)	0.0495
O(2)	0.5707(4)	−0.4405(3)	−0.1864(2)	0.0676
C(3)	0.9960(6)	−0.3232(4)	−0.1218(3)	0.0514
O(3)	1.0745(5)	−0.3642(3)	−0.0366(3)	0.0750
C(4)	0.7521(5)	−0.1963(4)	−0.4114(3)	0.0471
O(4)	0.6874(5)	−0.1632(3)	−0.4996(2)	0.0733
C(5)	1.0466(6)	−0.4456(4)	−0.3000(4)	0.0632
O(5)	1.1515(6)	−0.5559(3)	−0.3251(3)	0.0953
C(6)	0.6626(5)	−0.0562(3)	−0.2353(2)	0.0364
O(6)	0.6510(3)	0.0876(2)	−0.2809(2)	0.0424
C(7)	0.4735(4)	−0.0417(3)	−0.1624(2)	0.0361
C(8)	0.4731(5)	−0.1457(4)	−0.0638(3)	0.0438
C(9)	0.2919(5)	−0.1294(4)	−0.0003(3)	0.0439
C(10)	0.0993(4)	−0.0080(3)	−0.0329(2)	0.0371
C(11)	0.1030(5)	0.0970(4)	−0.1308(3)	0.0469
C(12)	0.2826(5)	0.0828(4)	−0.1943(3)	0.0449
C(13)	0.7881(6)	0.1310(4)	−0.3682(3)	0.0465
C(14)	0.7025(7)	0.3028(4)	−0.4045(4)	0.0609
H(8)	0.588(5)	−0.223(4)	−0.039(3)	
H(9)	0.299(5)	−0.194(4)	0.067(3)	
H(11)	−0.015(5)	0.171(4)	−0.154(3)	
H(12)	0.274(5)	0.148(4)	−0.261(3)	
H(131)	0.922(5)	0.096(4)	−0.335(3)	
H(132)	0.787(5)	0.079(4)	−0.429(3)	
H(141)	0.795(5)	0.341(4)	−0.460(3)	
H(142)	0.570(5)	0.334(4)	−0.439(3)	
H(143)	0.696(5)	0.349(4)	−0.345(3)	

phenyl ring to the other one is weak. A thermal vibration analysis of the diphenyl part was carried out using the rigid body model [18], and gave the following three latent roots of the libration tensors, 3.89 ° (6), 4.69 ° (6), and 10.02 ° (8); this last, the largest, angle is around a libration axis very close to the C(7)–C(10) line: actually the angle between those two directions is 2.34 ° (5). This result is similar to that obtained by Charbonneau and Delugeard.

The weak delocalization between the two subunits is confirmed by the comparison of the structural features of the carbenic moieties with the data for PhC(OMe)=Cr(CO)$_5$ [19]. The Cr=C, C–O(Me), O–Me and C–Ph bond lengths are remarkably similar in the two cases: namely, 2.051(4) vs. 2.04(3) Å, 1.321(3) vs. 1.33(2) Å, 1.446(4) vs. 1.46(3) Å and 1.485(4) vs. 1.47(4) Å.

Finally in order to confirm the weakness of this delocalization, mean planes were considered. The first one involves both phenyl rings and both carbenic carbon atoms; the largest deviation from the least squares planes is 0.05(2) Å. The second least squares plane involves Cr–C(6)–C(7)–O(6); the largest deviation from the plane is 0.04(1) Å. The angle between those two planes is 37 °, which means that there cannot be good π overlap. This deviation from planarity is due to strong steric hindrance between C(8) and its attached H with the C(2)O(2) carbonyl group attached to chromium. Two short intramolecular distances are found: C(2)–C(7) is equal to 3.101(9) Å and C(2)–C(8) is equal to 3.047(8) Å. C(7) and C(8) both belong to the phenyl ring.

Experimental

All preparations were carried out under N_2, using water-free solvents saturated with N_2. The *p*-biphenylenedilithium was prepared by a standard method [2].

Compound $(CO)_5CrC(OEt)(C_6H_4)_2(OEt)CCr(CO)_5$ *(1) (Table 6)*

p-Biphenylenedilithium in Et_2O (7.5 mmol) was added dropwise to a cold solution (0 °C) of 3.3 g of $Cr(CO)_6$ (15 mmol) in 200 ml Et_2O. The mixture which became deep yellow was stirred at 0 °C for 3 h and the ether then evaporated. The residue was dissolved in 75 ml of CH_2Cl_2, and 4 g of $[Et_3O][BF_4]$ were added in small portions. The CH_2Cl_2 was evaporated off and the residue extracted into 200 ml of Et_2O. After evaporation of the ether, the product was chromatographed on silica gel at −10 °C with 5/1 pentane/CH_2Cl_2 as eluant, to give 2.4 g of **1** as red

TABLE 6

EXPERIMENTAL DATA FOR THE X-RAY STUDY OF COMPOUND 1

Formula	$C_{28}H_{18}Cr_2O_{12}$
Molecular weight	650.30
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	6.644(2)
b, Å	9.491(3)
c, Å	12.468(3)
α, deg.	75.83(2)
β, deg.	85.98(3)
γ, deg.	69.29(3)
Z	1
D_{calc}, g.cm^{-3}	1.51
μ, cm^{-1}, no correction applied	8.01
Color	red
Habit	parallelepiped
Diffractometer	CAD 4-Nonius
Radiation	Mo-K_α
Monochromator	graphite
Method	θ–2θ
Scan range in	$1.20 + 0.345 \tan\theta$
2θ limits	3° to 50°
Temperature	room
Data collected	$\pm h \pm k\ l$
$F(000)$	297
Number of measured reflections	2884
Number of observed reflections ($I > 3\sigma(I)$)	1568
R	0.026
R_w	0.028

microcrystals. (Yield 50%), m. p. 105 °C. Analysis: Found: C, 51.42; H, 2.28; O, 29.03; Cr, 15.69. $C_{28}HCr_2O_{12}$ calc.: C, 51.71; H, 2.76; O, 29.52; Cr, 15.99%.

Compound $(CO)_5W{=}C(OEt)(C_6H_4)_2(OEt)C{=}W(CO)_5$ (2)

Compound **2** was prepared by the same method starting with 2.6 g of $W(CO)_6$ (7.5 mmol). Red microcrystals of **2** (2 g, 57%) were obtained. M.p. 108 °C. Analysis. Found: C, 36.69; H, 2.04; O, 21.13; W, 39.97. $C_{28}H_{18}O_{12}W_2$ calc.: C, 36.79; H, 1.96; O, 21.00; W, 40.23%.

Compound $(CO)_5Cr{=}C(NH_2)(C_6H_4)_2(NH_2)C{=}Cr(CO)_5$ (3)

Gaseous ammonia was bubbled through a solution of 300 mg of **1** (0.46 mmol) in 100 ml of Et_2O. The initially red solution rapidly became yellow. The solvent was evaporated off and the residue chromatographed on silica gel with pentane/CH_2Cl_2 as eluant. Recrystallization from 1/1 pentane/CH_2Cl_2 gave 190 mg of **3**. Yield 90%; 190 °C. Analysis, Found: C, 47.95; H, 2.09; N, 4.58. $C_{24}H_{13}Cr_2N_2O_{10}$ calc: C, 48.66; H, 2.04; N, 5.92%.

Compound $(CO)_5W{=}C(NH_2)(C_6H_4)_2(NH_2)C{=}W(CO)_5$ (4)

This complex was prepared in the same way as **3**. From 250 mg of **2** (0.27 mmol) in 100 ml Et_2O, 160 mg of **4** were isolated as a yellow powder. Yield 80%. Decomposition at 195 °C. Analysis. Found: C, 33.39; H, 1.47; N, 3.19. $C_{24}H_{12}N_2O_{10}W_2$ calc.: C, 33.67; H, 1.41; N, 3.27%.

Compound 5

$CH_3C{\equiv}CNEt_2$ (0.30 ml, 2.6 mmol, 3 equivalents) was added at 5 °C to a solution of 500 mg of **1** (0.77 mmol) in 5 ml of toluene. The solution became orange. After 30 min stirring (the reaction was monitored by TLC) the solvent was evaporated off and the residual oil is chromatographed on silica gel at −20 °C, with 1/1 pentane/CH_2Cl_2 as eluant. Recrystallization from 1/2 pentane/CH_2Cl_2 gave 340 mg of **5** as orange microcrystals. Yield 50%, m. p. 96–98 °C. Analysis. Found: C, 56.64; H, 5.14; O, 22.26; N, 3.16; Cr, 11.98. $C_{38}H_{34}Cr_2N_2O_{12}$ calc.: C, 57.80; H, 5.08; O, 22.00; N, 3.21; Cr, 11.91%.

Compound 6 and compound 7

These were prepared as described for **5** above. Use of 500 mg of **2** (0.55 mmol), 0.20 ml of $CH_3C{\equiv}CNEt_2$ (3 equivalents) gave (a) 10 mg of **7** (pentane/CH_2Cl_2 3/2). Yield < 2%, m. p. 58 °C, and (b) 310 mg of **6** (pentane/CH_2Cl_2 1.1). Yield 50%. m. p.: 140 °C. Analysis. Found: C, 44.17; H, 3.95; O, 16.58; N, 2.37; W, 32.24. $C_{42}H_{44}N_2O_{12}W_2$ calc.: C, 44.38; H, 3.90; O, 16.89; N, 2.46; W, 32.35%.

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