

Table 2. Selected geometric parameters (Å, °)

Sn(1)—O(B)	2.100 (2)	Sn(2)—C(212)	2.102 (5)
Sn(1)—O(110)	2.090 (3)	O(B)—Li	2.342 (9)
Sn(1)—O(120)	2.092 (3)	O(110)—C(110)	1.427 (6)
Sn(1)—C(116)	2.113 (5)	O(120)—C(120)	1.419 (7)
Sn(1)—C(122)	2.107 (5)	O(120)—Li	1.884 (9)
Sn(2)—O(B)	2.088 (4)	O(210)—C(210)	1.425 (6)
Sn(2)—O(210)	2.091 (3)	O(210)—Li	1.89 (1)
O(B)—Sn(1)—O(110)	83.2 (1)	C(212)—Sn(2)—C(212')	125.0 (3)
O(B)—Sn(1)—O(120)	84.07 (9)	Sn(1)—O(B)—Sn(1')	119.5 (2)
O(B)—Sn(1)—C(116)	116.8 (2)	Sn(1)—O(B)—Sn(2)	120.3 (1)
O(B)—Sn(1)—C(122)	117.2 (2)	Sn(1)—O(B)—Li	89.5 (2)
O(110)—Sn(1)—O(120)	167.3 (1)	Sn(2)—O(B)—Li	90.1 (3)
O(110)—Sn(1)—C(116)	81.0 (2)	Li—O(B)—Li'	180 (1)
O(110)—Sn(1)—C(122)	105.2 (2)	Sn(1)—O(110)—C(110)	113.8 (3)
O(120)—Sn(1)—C(116)	104.1 (2)	Sn(1)—O(120)—C(120)	114.0 (3)
O(120)—Sn(1)—C(122)	81.3 (2)	Sn(1)—O(120)—Li	103.9 (3)
C(116)—Sn(1)—C(122)	126.0 (2)	C(120)—O(120)—Li	124.9 (4)
O(B)—Sn(2)—O(210)	83.95 (9)	Sn(2)—O(210)—C(210)	113.8 (3)
O(B)—Sn(2)—C(212)	117.5 (1)	Sn(2)—O(210)—Li	103.9 (3)
O(210)—Sn(2)—O(210')	167.9 (2)	C(210)—O(210)—Li	126.8 (4)
O(210)—Sn(2)—C(212)	81.1 (2)		

One Sn-atom position was solved using the Patterson heavy-atom method. The remaining atoms were located using *DIRDIF* (Beurskens *et al.*, 1984) and in succeeding difference Fourier syntheses. It was not possible to differentiate the hydroxy and the two methyl groups of the 2-phenylpropanol solvent molecule. Hence, these three atoms were refined as C atoms without attached H atoms. All other H atoms were located and included in the structure-factor calculations, but their positions were not refined. The structure was refined by full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as per the Killean & Lawrence (1969) method with the terms 0.20 and 1.0. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). The highest peak in the final difference Fourier map had a height of 0.53 \AA^{-3} with an estimated error based on ΔF (Cruickshank, 1945) of 0.08. All calculations were performed on a VAX computer using *SDP* (Enraf-Nonius, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 2503–2508

Three α,β -Unsaturated (Carbene)pentacarbonylchromium Complexes

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Abstract

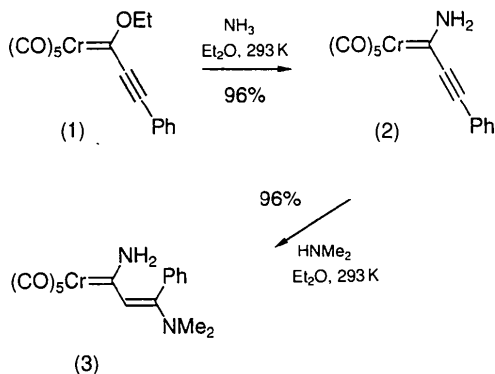
The syntheses and crystal structures of [(2*E*)-1-amino-3-dimethylamino-3-phenylpropen-1-ylidene]pentacarbonylchromium, $[\text{Cr}(\text{C}_{11}\text{H}_{14}\text{N}_2)(\text{CO})_5]$, pentacarbonyl[(2*E*)-3-dibenzylamino-1-ethoxy-6,6-dimethylhept-2-en-4-ynylidene]chromium, $[\text{Cr}(\text{C}_{25}\text{H}_{29}\text{NO})(\text{CO})_5]$, and pentacarbonyl[(4-dibenzylamino-5,5-dimethyl-2,5-dihydro-2-furylidene)chromium, $[\text{Cr}(\text{C}_{20}\text{H}_{21}\text{NO})(\text{CO})_5]$, are reported. All compounds show significant π delocalization over the carbene fragment.

Comment

α,β -Unsaturated (carbene)chromium complexes have become important reagents in synthetic organic chemistry. With appropriate substituents at the carbene C atom and/or the vinyl terminus, they react with alkynes in a number of ways to give various ring systems. The addition of ammonia to (alkynylcarbene)chromium complexes leads either to [(*Z*)-2-aminoethynyl]carbene complexes or to (1-aminoethynyl)carbene complexes; this can be controlled by temperature variations (Stein, Duetsch, Pohl, Herbst-Irmer & de Meijere, 1993).

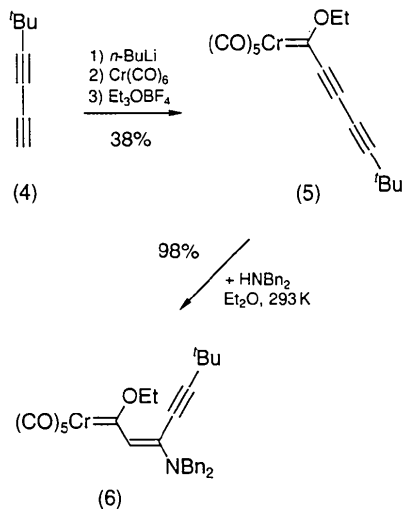
The reaction of (1-ethoxy-3-phenylpropynylidene)-pentacarbonylchromium, (1), with ammonia afforded exclusively the substitution product (2) in 96% yield at

room temperature (Stein, 1993). Michael-type addition of dimethylamine yielded [(*E*)-1-amino-3-dimethylamino-3-phenylpropen-1-ylidene]pentacarbonylchromium, (3), in 96% yield as yellow crystals. The



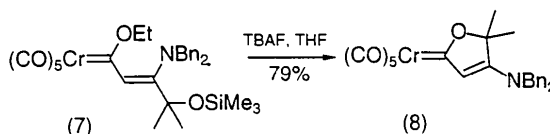
structure was determined by X-ray crystallography to confirm the *E* configuration of the C2=C3 double bond. The bond lengths and angles agree with values found for pentacarbonyl{(2-dimethylaminoethenyl)[(methoxy)phenylmethylamino]carbene}chromium (Wienand, Reissig, Fischer & Hofman, 1989). The planar environment of N1 and N4 indicates π delocalization over the N atoms. The mean deviation from the least-squares plane through Cr1, C1, N1, C2, C3, C31 and N4 is 0.193 Å.

The first 1,3-diynechromium complex, (5), was synthesized from the hexadiyne (4) in 38% yield (Funke & de Meijere, 1995). The reaction of the complex (5) with dibenzylamine gave a selective Michael-type addition to the C3 atom of (5) and only the *E* isomer of the orange coloured complex (6) (98% yield) was formed; this had to be proved by X-ray crystallography. The ethoxyethenylcarbene ligand is almost planar (the mean deviation from the least-squares plane through Cr, C1, O1, N1, C2, C3 and C4 is 0.055 Å). The C4=C5 bond distance of 1.195 (3) Å is typical for a C=C double bond.



This new functionalized α,β -unsaturated (carbene)chromium complex (6) is useful for cycloaddition to alkynes, yielding various ring systems with interesting functional groups (Funke & de Meijere, 1995).

Treatment of the dibenzylamino(trimethylsilyloxy)-substituted complex (7) with tetra-*n*-butylammonium fluoride (TBAF) in THF afforded pentacarbonyl(4-dibenzylamino-5,5-dimethyl-2,5-dihydro-2-furylidene)chromium, (8), in 79% yield, by intramolecular substitution of the ethoxy group (Stein, Duetsch, Noltemeyer & de Meijere, 1993; Lattuada, Licandro, Maiorana, Molinari & Papagni, 1991; Christophers & Dötz, 1993). The structure assignment was confirmed by the X-ray crystal structure determination.



Compound (8) showed very low reactivity towards electrophilic addition of various reagents to the formal C4=C5 double bond. The crystal structure of (8) shows a five-membered central planar ring (the mean deviation from least-squares plane through Cr1, C1, O2, C3, C4, C5 and N6 is 0.015 Å). This planarity, the planar coordination environment around N6, and the bond lengths found for N6—C4, C1—C5 and C1—Cr1 indicate delocalization of the double bond within the core unit.

The carbene fragment in (3) is less planar than in (6) and (8). The shortest C_{carbene}—C_{olefin} distance was found for (8) and the longest for (3); the shortest C=C double bond was observed in (3). This indicates that the degree for π delocalization is highest in (8) and lowest in (3). However, the C_{carbene}—Cr distances are comparable for (3) and (6), but it is significantly shorter in (8), compared with (6) and other O-substituted complexes {e.g. pentacarbonyl[(*E*)-3-(diisopropylamino)-1-ethoxy-3-phenylpropylidene]chromium (Duetsch *et al.*, 1992)}.

In general, the C_{carbene}—Cr distances are shorter for the carbene complexes with O substituents than for

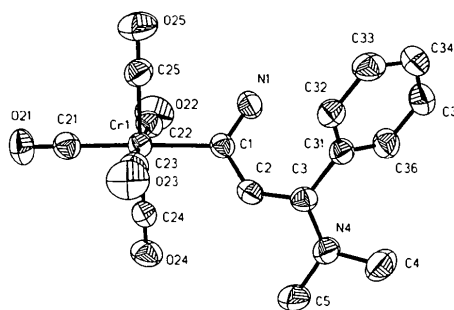


Fig. 1. Structure of (3) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

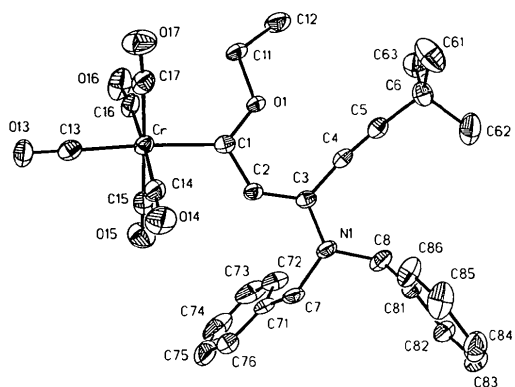


Fig. 2. Structure of (6) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

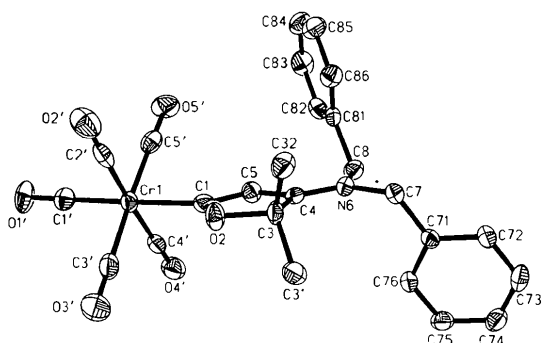


Fig. 3. Structure of (8) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

the carbene complexes with N substituents [*cf.* pentacarbonyl[cyclohexylamino-(1-methoxyvinyl)carbene]chromium (Huttner & Lange, 1970), pentacarbonyl[(*Z*)-dimethoxyvinyl]methoxycarbenechromium (Dötz, Kuhn & Thewalt, 1985), pentacarbonyl[(*E*)-3-(dimethylamino)-1-methoxypropylidene]chromium (Lattuada *et al.*, 1988)].

All three compounds show almost ideal octahedral coordination around the Cr atom. The C—Cr distance of the carbonyl group *trans* to the carbene centre is between 0.02 and 0.04 Å shorter than the C—Cr distances to the other carbonyl ligands, as is usual in Fischer carbene complexes (Fischer, 1974).

Experimental

Compound (3)

Crystal data

[Cr(C₁₁H₁₄N₂)(CO)₅]

M_r = 366.29

Orthorhombic

*P*2₁2₁2

a = 12.658 (1) Å

b = 14.186 (2) Å

c = 9.527 (1) Å

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 68 reflections

θ = 10–12.5°

μ = 0.695 mm⁻¹

T = 293 (2) K

V = 1710.7 (3) Å³

Z = 4

D_x = 1.422 Mg m⁻³

Block

0.6 × 0.3 × 0.3 mm

Yellow

Data collection

Stoe Huber four-circle

diffractometer

Profile data from 2θ/ω scans

Absorption correction:

ψ scan (North, Phillips & Mathews, 1968)

T_{min} = 0.845, *T_{max}* =

0.952

7116 measured reflections

3974 independent reflections

3009 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0362

θ_{max} = 27.60°

h = -16 → 16

k = -18 → 18

l = -12 → 12

3 standard reflections

frequency: 90 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0405

wR(*F*²) = 0.1055

S = 1.033

3974 reflections

226 parameters

w = 1/[σ²(*F_o*²) + (0.0483*P*)² + 0.4169*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.688 e Å⁻³

Δρ_{min} = -0.236 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

= 0.48 (3)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (3)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cr1	0.87583 (4)	0.15650 (3)	0.03132 (5)	0.04188 (13)
C21	0.9659 (2)	0.1362 (2)	-0.1203 (3)	0.0495 (8)
O21	1.0205 (2)	0.1217 (2)	-0.2135 (3)	0.0679 (7)
C22	0.9238 (3)	0.2816 (3)	0.0542 (4)	0.0545 (8)
O22	0.9528 (2)	0.3567 (2)	0.0685 (4)	0.0917 (10)
C23	0.8207 (2)	0.0329 (2)	0.0144 (4)	0.0521 (7)
O23	0.7866 (2)	-0.0407 (2)	-0.0015 (3)	0.0769 (8)
C24	0.9835 (3)	0.1201 (2)	0.1576 (3)	0.0462 (7)
O24	1.0492 (2)	0.1010 (2)	0.2335 (3)	0.0651 (7)
C25	0.7683 (3)	0.1985 (3)	-0.0880 (4)	0.0538 (8)
O25	0.7020 (2)	0.2248 (2)	-0.1609 (3)	0.0851 (9)
C1	0.7731 (2)	0.1735 (2)	0.2044 (3)	0.0410 (6)
N1	0.7114 (2)	0.2488 (2)	0.2130 (3)	0.0545 (7)
C2	0.7715 (2)	0.1068 (2)	0.3165 (3)	0.0452 (7)
C3	0.7027 (2)	0.0964 (2)	0.4262 (3)	0.0418 (6)
N4	0.7273 (2)	0.0434 (2)	0.5395 (3)	0.0527 (6)
C4	0.6507 (3)	0.0060 (3)	0.6390 (4)	0.0653 (10)
C5	0.8342 (3)	0.0053 (3)	0.5561 (4)	0.0738 (12)
C31	0.5937 (2)	0.1375 (2)	0.4242 (3)	0.0416 (6)
C32	0.5257 (2)	0.1143 (2)	0.3165 (3)	0.0454 (7)
C33	0.4240 (2)	0.1487 (3)	0.3147 (4)	0.0543 (8)
C34	0.3899 (3)	0.2079 (3)	0.4193 (4)	0.0628 (9)
C35	0.4573 (3)	0.2333 (3)	0.5253 (4)	0.0627 (9)
C36	0.5600 (2)	0.1987 (3)	0.5292 (4)	0.0534 (7)

Table 2. Geometric parameters (Å, °) for (3)

Cr1—C21	1.862 (3)	C1—C2	1.427 (4)
Cr1—C25	1.871 (3)	C2—C3	1.368 (4)
Cr1—C22	1.889 (4)	C3—N4	1.352 (4)
Cr1—C24	1.890 (3)	C3—C31	1.498 (4)
Cr1—C23	1.895 (3)	N4—C4	1.456 (4)
Cr1—C1	2.114 (3)	N4—C5	1.466 (4)

C21—O21	1.144 (4)	C31—C32	1.380 (4)
C22—O22	1.135 (4)	C31—C36	1.391 (4)
C23—O23	1.139 (4)	C32—C33	1.377 (4)
C24—O24	1.135 (4)	C33—C34	1.373 (5)
C25—O25	1.151 (4)	C34—C35	1.370 (5)
C1—N1	1.326 (4)	C35—C36	1.389 (4)
C21—Cr1—C25	91.32 (15)	O25—C25—Cr1	179.6 (3)
C21—Cr1—C22	92.20 (15)	N1—C1—C2	118.7 (3)
C25—Cr1—C22	90.2 (2)	N1—C1—Cr1	120.1 (2)
C21—Cr1—C24	90.59 (14)	C2—C1—Cr1	121.1 (2)
C25—Cr1—C24	176.9 (2)	C3—C2—C1	130.7 (3)
C22—Cr1—C24	87.24 (15)	N4—C3—C2	121.5 (3)
C21—Cr1—C23	90.94 (14)	N4—C3—C31	116.0 (3)
C25—Cr1—C23	88.58 (15)	C2—C3—C31	122.3 (3)
C22—Cr1—C23	176.67 (15)	C3—N4—C4	124.7 (3)
C24—Cr1—C23	93.84 (14)	C3—N4—C5	120.2 (3)
C21—Cr1—C1	177.66 (14)	C4—N4—C5	114.2 (3)
C25—Cr1—C1	89.44 (13)	C32—C31—C36	119.5 (3)
C22—Cr1—C1	90.02 (13)	C32—C31—C3	119.4 (3)
C24—Cr1—C1	88.75 (12)	C36—C31—C3	121.1 (3)
C23—Cr1—C1	86.86 (13)	C33—C32—C31	120.5 (3)
O21—C21—Cr1	178.5 (3)	C34—C33—C32	120.1 (3)
O22—C22—Cr1	179.7 (3)	C35—C34—C33	120.0 (3)
O23—C23—Cr1	177.1 (3)	C34—C35—C36	120.6 (4)
O24—C24—Cr1	177.9 (3)	C35—C36—C31	119.2 (3)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (6)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
Cr	0.63406 (3)	0.50677 (3)	0.75943 (3)	0.02443 (13)
C13	0.6685 (2)	0.6514 (2)	0.8889 (2)	0.0297 (5)
O13	0.6885 (2)	0.74113 (15)	0.96847 (14)	0.0393 (4)
C14	0.7239 (2)	0.5955 (2)	0.6784 (2)	0.0311 (5)
O14	0.7779 (2)	0.6511 (2)	0.6308 (2)	0.0479 (5)
C15	0.7854 (2)	0.4658 (2)	0.8203 (2)	0.0320 (5)
O15	0.8746 (2)	0.4416 (2)	0.8596 (2)	0.0490 (5)
C16	0.5491 (2)	0.4244 (2)	0.8480 (2)	0.0339 (6)
O16	0.5026 (2)	0.3813 (2)	0.9082 (2)	0.0546 (5)
C17	0.4823 (2)	0.5479 (2)	0.7032 (2)	0.0329 (5)
O17	0.3925 (2)	0.5786 (2)	0.6743 (2)	0.0516 (5)
O1	0.50015 (13)	0.26281 (14)	0.55122 (13)	0.0305 (4)
C11	0.3802 (2)	0.2641 (2)	0.5891 (2)	0.0357 (6)
C12	0.2924 (2)	0.1408 (2)	0.5229 (3)	0.0491 (7)
C1	0.6066 (2)	0.3494 (2)	0.6094 (2)	0.0241 (5)
C2	0.7111 (2)	0.3254 (2)	0.5553 (2)	0.0245 (5)
C3	0.7123 (2)	0.2356 (2)	0.4511 (2)	0.0240 (5)
C4	0.6009 (2)	0.1467 (2)	0.3746 (2)	0.0259 (5)
C5	0.5158 (2)	0.0697 (2)	0.3021 (2)	0.0268 (5)
C6	0.4174 (2)	-0.0247 (2)	0.2070 (2)	0.0336 (5)
C61	0.3244 (3)	0.0369 (3)	0.1551 (3)	0.0612 (8)
C62	0.4863 (3)	-0.0903 (3)	0.1126 (2)	0.0544 (7)
C63	0.3474 (2)	-0.1188 (2)	0.2535 (2)	0.0429 (6)
N1	0.8239 (2)	0.2279 (2)	0.4122 (2)	0.0276 (4)
C7	0.9442 (2)	0.3127 (2)	0.4803 (2)	0.0315 (5)
C71	1.0016 (2)	0.2868 (2)	0.5874 (2)	0.0323 (5)
C72	0.9537 (2)	0.1792 (2)	0.6076 (2)	0.0410 (6)
C73	1.0105 (3)	0.1574 (3)	0.7045 (3)	0.0604 (9)
C74	1.1155 (3)	0.2405 (4)	0.7820 (3)	0.0734 (11)
C75	1.1628 (3)	0.3474 (4)	0.7632 (3)	0.0687 (10)
C76	1.1062 (2)	0.3714 (3)	0.6669 (2)	0.0473 (7)
C8	0.8345 (2)	0.1296 (2)	0.3082 (2)	0.0324 (5)
C81	0.8739 (2)	0.1766 (2)	0.2138 (2)	0.0291 (5)
C82	0.9662 (2)	0.1338 (2)	0.1559 (2)	0.0348 (6)
C83	1.0025 (2)	0.1752 (2)	0.0688 (2)	0.0412 (6)
C84	0.9479 (3)	0.2610 (2)	0.0389 (2)	0.0463 (7)
C85	0.8559 (3)	0.3042 (2)	0.0954 (2)	0.0518 (7)
C86	0.8186 (3)	0.2618 (2)	0.1821 (2)	0.0422 (6)

Compound (6)*Crystal data*[Cr(C₂₅H₂₉NO)(CO)₅]M_r = 551.54

Triclinic

P $\bar{1}$

a = 10.834 (2) Å

b = 11.745 (2) Å

c = 12.222 (2) Å

α = 108.09 (2)°

β = 98.22 (2)°

γ = 100.11 (2)°

V = 1422.6 (4) Å³

Z = 2

D_x = 1.288 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 59 reflections

θ = 10–12.5°

μ = 0.444 mm⁻¹

T = 153 (2) K

Block

0.9 × 0.4 × 0.4 mm

Orange

Data collection

Stoe Huber four-circle diffractometer

Profile data from 2θ/ω scans

Absorption correction:

ψ scan (North, Phillips

& Mathews, 1968)

T_{min} = 0.643, T_{max} =

0.742

4192 measured reflections

3700 independent reflections

3366 observed reflections

[I > 2σ(I)]

*Refinement*Refinement on F²R[F² > 2σ(F²)] = 0.0319wR(F²) = 0.0853

S = 1.042

3700 reflections

347 parameters

w = 1/[σ²(F_o²) + (0.0409P)² + 1.0072P]where P = (F_o² + 2F_c²)/3R_{int} = 0.0392θ_{max} = 22.51°

h = -11 → 11

k = -12 → 12

l = -11 → 13

3 standard reflections

frequency: 90 min

intensity decay: none

(Δ/σ)_{max} = 0.001Δρ_{max} = 0.279 e Å⁻³Δρ_{min} = -0.310 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 4. Geometric parameters (Å, °) for (6)

Cr—C13	1.862 (3)	C6—C61	1.517 (3)
Cr—C17	1.890 (3)	C6—C63	1.530 (3)
Cr—C14	1.891 (2)	C6—C62	1.542 (4)
Cr—C16	1.891 (3)	N1—C7	1.450 (3)
Cr—C15	1.903 (3)	N1—C8	1.462 (3)
Cr—C1	2.101 (2)	C7—C71	1.508 (3)
C13—O13	1.152 (3)	C71—C76	1.381 (3)
C14—O14	1.142 (3)	C71—C72	1.388 (3)
C15—O15	1.138 (3)	C72—C73	1.372 (4)
C16—O16	1.140 (3)	C73—C74	1.368 (5)
C17—O17	1.142 (3)	C74—C75	1.370 (5)
O1—C1	1.332 (3)	C75—C76	1.379 (4)
O1—C11	1.442 (3)	C8—C81	1.507 (3)
C11—C12	1.491 (3)	C81—C86	1.377 (3)
C1—C2	1.418 (3)	C81—C82	1.382 (3)
C2—C3	1.382 (3)	C82—C83	1.378 (3)
C3—N1	1.368 (3)	C83—C84	1.369 (4)
C3—C4	1.431 (3)	C84—C85	1.373 (4)
C4—C5	1.195 (3)	C85—C86	1.383 (4)
C5—C6	1.466 (3)		
C13—Cr—C17	88.20 (10)	C5—C4—C3	173.0 (2)
C13—Cr—C14	89.19 (9)	C4—C5—C6	175.9 (2)
C17—Cr—C14	89.44 (10)	C5—C6—C61	109.1 (2)
C13—Cr—C16	88.05 (9)	C5—C6—C63	110.2 (2)
C17—Cr—C16	91.64 (10)	C61—C6—C63	110.9 (2)
C14—Cr—C16	177.00 (10)	C5—C6—C62	107.4 (2)
C13—Cr—C15	90.83 (10)	C61—C6—C62	110.0 (2)
C17—Cr—C15	178.32 (9)	C63—C6—C62	109.2 (2)
C14—Cr—C15	91.91 (10)	C3—N1—C7	120.7 (2)

C16—Cr—C15	86.95 (10)	C3—N1—C8	123.9 (2)	C2'	0.7618 (4)	0.7852 (3)	0.6926 (3)	0.0331 (10)
C13—Cr—C1	175.88 (9)	C7—N1—C8	115.1 (2)	O2'	0.7947 (3)	0.8302 (2)	0.6383 (3)	0.0532 (9)
C17—Cr—C1	93.35 (9)	N1—C7—C71	114.7 (2)	C3'	0.6487 (4)	0.7717 (2)	0.8814 (3)	0.0372 (11)
C14—Cr—C1	87.01 (9)	C76—C71—C72	118.8 (2)	O3'	0.6135 (4)	0.8092 (2)	0.9450 (3)	0.0643 (11)
C16—Cr—C1	95.71 (9)	C76—C71—C7	119.2 (2)	C4'	0.6556 (4)	0.6311 (3)	0.8578 (3)	0.0301 (10)
C15—Cr—C1	87.71 (9)	C72—C71—C7	121.9 (2)	O4'	0.6289 (3)	0.5835 (2)	0.9097 (2)	0.0445 (8)
O13—C13—Cr	179.1 (2)	C73—C72—C71	120.3 (3)	C5'	0.7698 (4)	0.6480 (2)	0.6711 (3)	0.0314 (10)
O14—C14—Cr	178.7 (2)	C74—C73—C72	120.7 (3)	O5'	0.8142 (3)	0.6116 (2)	0.6090 (2)	0.0466 (8)
O15—C15—Cr	178.0 (2)	C73—C74—C75	119.4 (3)	C1	0.8917 (4)	0.7019 (2)	0.8527 (3)	0.0285 (10)
O16—C16—Cr	175.3 (2)	C74—C75—C76	120.7 (3)	O2	0.9550 (2)	0.7580 (2)	0.8986 (2)	0.0328 (7)
O17—C17—Cr	176.3 (2)	C75—C76—C71	120.1 (3)	C3	1.0895 (3)	0.7393 (2)	0.9465 (3)	0.0271 (9)
C1—O1—C11	122.0 (2)	N1—C8—C81	112.8 (2)	C31	1.0892 (4)	0.7566 (3)	1.0651 (3)	0.0345 (10)
O1—C11—C12	107.2 (2)	C86—C81—C82	118.3 (2)	C32	1.1870 (4)	0.7845 (2)	0.8875 (3)	0.0346 (10)
O1—C1—C2	110.7 (2)	C86—C81—C8	121.3 (2)	C4	1.0958 (4)	0.6609 (2)	0.9212 (3)	0.0238 (9)
O1—C1—Cr	129.51 (14)	C82—C81—C8	120.5 (2)	C5	0.9761 (4)	0.6421 (2)	0.8667 (3)	0.0281 (10)
C2—C1—Cr	119.75 (15)	C83—C82—C81	121.1 (2)	N6	1.2006 (3)	0.6187 (2)	0.9466 (2)	0.0267 (8)
C3—C2—C1	129.4 (2)	C84—C83—C82	120.1 (2)	C7	1.3241 (3)	0.6392 (2)	1.0096 (3)	0.0289 (10)
N1—C3—C2	120.9 (2)	C83—C84—C85	119.5 (2)	C71	1.3421 (4)	0.6019 (2)	1.1161 (3)	0.0252 (9)
N1—C3—C4	114.7 (2)	C84—C85—C86	120.4 (3)	C72	1.4710 (4)	0.5921 (2)	1.1635 (3)	0.0314 (10)
C2—C3—C4	124.4 (2)	C81—C86—C85	120.6 (2)	C73	1.4915 (4)	0.5598 (2)	1.2622 (3)	0.0366 (11)
				C74	1.3825 (4)	0.5362 (2)	1.3141 (3)	0.0365 (11)
				C75	1.2545 (4)	0.5447 (2)	1.2674 (3)	0.0325 (10)
				C76	1.2333 (4)	0.5782 (2)	1.1691 (3)	0.0299 (10)
				C8	1.1928 (4)	0.5448 (2)	0.9119 (3)	0.0292 (10)
				C81	1.1916 (3)	0.5346 (2)	0.7915 (3)	0.0255 (9)
				C82	1.1251 (4)	0.4775 (2)	0.7438 (3)	0.0327 (10)
				C83	1.1270 (4)	0.4656 (3)	0.6348 (3)	0.0409 (12)
				C84	1.1940 (4)	0.5125 (3)	0.5728 (3)	0.0390 (11)
				C85	1.2597 (4)	0.5693 (2)	0.6195 (3)	0.0387 (11)
				C86	1.2587 (4)	0.5811 (2)	0.7291 (3)	0.0330 (10)

Compound (8)*Crystal data*[Cr(C₂₀H₂₁NO)(CO)₅] $M_r = 483.43$

Monoclinic

 $P2_1/c$ $a = 9.950 (1) \text{ \AA}$ $b = 18.856 (4) \text{ \AA}$ $c = 12.522 (2) \text{ \AA}$ $\beta = 94.30 (1)^\circ$ $V = 2342.7 (7) \text{ \AA}^3$ $Z = 4$ $D_x = 1.371 \text{ Mg m}^{-3}$ *Data collection*

Stoe Huber four-circle diffractometer

Profile data from $2\theta/\omega$ scans

Absorption correction:

none

6685 measured reflections

3021 independent reflections

2252 observed reflections

 $[I > 2\sigma(I)]$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0428$ $wR(F^2) = 0.1124$ $S = 1.074$

3020 reflections

300 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 3.9566P]$ where $P = (F_o^2 + 2F_c^2)/3$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 65 reflections

 $\theta = 10\text{--}12.5^\circ$ $\mu = 0.528 \text{ mm}^{-1}$ $T = 153 (2) \text{ K}$

Block

 $0.5 \times 0.5 \times 0.4 \text{ mm}$

Brown

 $R_{int} = 0.0382$ $\theta_{max} = 22.53^\circ$ $h = -10 \rightarrow 10$ $k = -20 \rightarrow 20$ $l = -13 \rightarrow 13$

3 standard reflections

frequency: 90 min

intensity decay: 2%

 $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.337 \text{ e \AA}^{-3}$ $\Delta\rho_{min} = -0.349 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 6. Selected geometric parameters (\AA , $^\circ$) for (8)

Cr1—C1'	1.862 (4)	C1—C5	1.409 (6)
Cr1—C2'	1.879 (5)	O2—C3	1.468 (4)
Cr1—C5'	1.883 (5)	C3—C4	1.514 (6)
Cr1—C4'	1.887 (5)	C3—C31	1.521 (5)
Cr1—C3'	1.902 (5)	C3—C32	1.524 (5)
Cr1—C1	2.047 (4)	C4—N6	1.331 (5)
C1'—O1'	1.154 (4)	C4—C5	1.374 (5)
C2'—O2'	1.150 (5)	N6—C8	1.460 (5)
C3'—O3'	1.139 (5)	N6—C7	1.462 (5)
C4'—O4'	1.151 (5)	C7—C71	1.507 (5)
C5'—O5'	1.149 (5)	C8—C81	1.518 (5)
C1—O2	1.339 (5)		
C1'—Cr1—C2'	89.4 (2)	O2—C1—C5	108.8 (3)
C1'—Cr1—C5'	92.3 (2)	O2—C1—Cr1	122.5 (3)
C2'—Cr1—C5'	87.6 (2)	C5—C1—Cr1	128.7 (3)
C1'—Cr1—C4'	93.4 (2)	C1—O2—C3	111.8 (3)
C2'—Cr1—C4'	177.0 (2)	O2—C3—C4	101.5 (3)
C5'—Cr1—C4'	91.2 (2)	O2—C3—C31	106.2 (3)
C1'—Cr1—C3'	91.0 (2)	C4—C3—C31	114.6 (3)
C2'—Cr1—C3'	91.4 (2)	O2—C3—C32	105.1 (3)
C5'—Cr1—C3'	176.6 (2)	C4—C3—C32	114.0 (3)
C4'—Cr1—C3'	89.6 (2)	C31—C3—C32	113.7 (3)
C1'—Cr1—C1	178.7 (2)	N6—C4—C5	126.8 (4)
C2'—Cr1—C1	90.4 (2)	N6—C4—C3	125.3 (3)
C5'—Cr1—C1	86.5 (2)	C5—C4—C3	107.9 (3)
C4'—Cr1—C1	86.8 (2)	C4—C5—C1	110.0 (4)
C3'—Cr1—C1	90.2 (2)	C4—N6—C8	118.4 (3)
O1'—C1'—Cr1	177.5 (4)	C4—N6—C7	125.6 (3)
O2'—C2'—Cr1	176.7 (4)	C8—N6—C7	115.9 (3)
O3'—C3'—Cr1	179.0 (4)	N6—C7—C71	113.2 (3)
O4'—C4'—Cr1	178.5 (3)	N6—C8—C81	114.3 (3)
O5'—C5'—Cr1	177.7 (3)		

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (8)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cr1	0.70411 (6)	0.70898 (4)	0.77426 (5)	0.0263 (2)
C1'	0.5349 (4)	0.7144 (2)	0.7003 (3)	0.0307 (10)
O1'	0.4313 (3)	0.7203 (2)	0.6532 (2)	0.0466 (8)

Data for all three compounds were collected using a profile-fitting method (Clegg, 1981). The crystals of (6) and (8) were cooled using a locally built low-temperature device (Kotke, 1993). The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 . All H atoms were included in calculated positions and refined using a riding model, except the H atoms at N1 of compound (3), which were refined with distance restraints. The isotropic

displacement parameters were set to 1.2 times (1.5 for methyl groups) the equivalent isotropic displacement parameters of the atoms to which the H atoms are bonded. For all methyl groups one torsion angle was refined. Compound (3) was refined as a racemic twin using the method of Flack (1983).

For all compounds, data collection: *DIF4* (Stoe & Cie, 1988a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1988b); program(s) used to solve structures: *SHELX90* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cationic Rhenium–Platinum Complex: *fac*-Tricarbonylrhenium-bis[μ -methylaminobis(difluorophosphine)]-triphenylphosphineplatinum Trifluoromethanesulfonate

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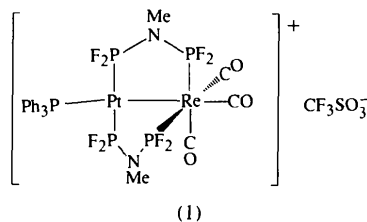
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Abstract

The title compound, *fac*-tricarbonyl- $1\kappa^3C$ -bis[μ -methylaminobis(difluorophosphine)- $1\kappa P:2\kappa P'$]triphenylphosphine- $2\kappa P$ -platinumrhenium (*Pt*—*Re*) trifluoromethanesulfonate, [PtRe(CO)₃(CH₃F₄NP₂)₂(C₁₈H₁₅P)]·CF₃SO₃, exhibits distorted octahedral and square-planar coordination about the Re and Pt atoms, respectively. A Pt—Re single bond of length 2.818 (1) Å is present.

Comment

Previous studies of the 'metalloligands' CpMCl{ η^1 -MeN(PF₂)₂}₂ (*M* = Fe, Ru) and *fac*-ReBr(CO)₃{ η^1 -L₂}₂ [L₂ = MeN(PF₂)₂, CH₂(PMe₂)₂ (dmpm)] (Mague & Lin, 1992, 1994; Mague, 1994) have shown them to be useful for the directed synthesis of heterobimetallic complexes. To date, the reactions of these complexes have proven quite limited; in an attempt to increase reactivity, the weakly bound Br ligand in *fac*-Re(CO)₃{ μ -MeN(PF₂)₂}₂PtBr(PPh₃), (2) (Mague & Lin, 1994), was removed by reacting with silver trifluoromethanesulfonate to give the title compound, (1). Little increase in the reactivity of (1) over its precursor was seen, suggesting that the trifluoromethanesulfonate ion might be coordinated in place of the Br atom. As spectroscopic data were inconclusive on this point, the structure of (1) was determined by X-ray analysis.



In the crystal form, (1) consists of well separated [Re(CO)₃{ μ -MeN(PF₂)₂}₂Pt{P(C₆H₅)₃}]⁺ cations and CF₃SO₃⁻ anions. Both ions have crystallographically imposed mirror symmetry and while the displacement