

**fac-Tricarbonylchloro(1,10-phenanthroline)-rhenium(I)****Salim F. Haddad,<sup>a\*</sup> Jason A. Marshall,<sup>b</sup> G. Full name? A. Crosby<sup>b</sup> and Brendan Twamley<sup>c</sup>**<sup>a</sup>Department of Chemistry, The University of Jordan, Amman 11942, Jordan, <sup>b</sup>Department of Chemistry, Washington State University, Pullman, WA 99164, USA, and <sup>c</sup>University Research Office, University of Idaho, Moscow, ID 83844, USA

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**Key indicators**

Single-crystal X-ray study

T = 203 K

Mean  $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$ 

R factor = 0.027

wR factor = 0.067

Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Re}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{CO})_3\text{Cl}]$ , contains isolated molecular units. Rhenium(I) is six-coordinated by the two N atoms of 1,10-phenanthroline, three carbonyls and one chloride anion. The coordination sphere is a distorted octahedron, with the chloride anion *trans* to one of the carbonyls. There is a significant *trans* influence, which lengthens one of the Re—C bonds by *ca.* 0.05 Å. The bidentate 1,10-phenanthroline deviates slightly from planarity, with a dihedral angle between its two heterocyclic rings of 5.5 (3)°, and is folded away from the chloride anion. The Re(I) atom lies 0.192 (3) Å from the least-squares plane of 1,10-phenanthroline. There are no  $\pi$  ring interactions between adjacent 1,10-phenanthroline rings.

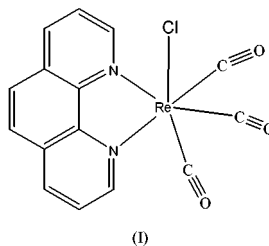
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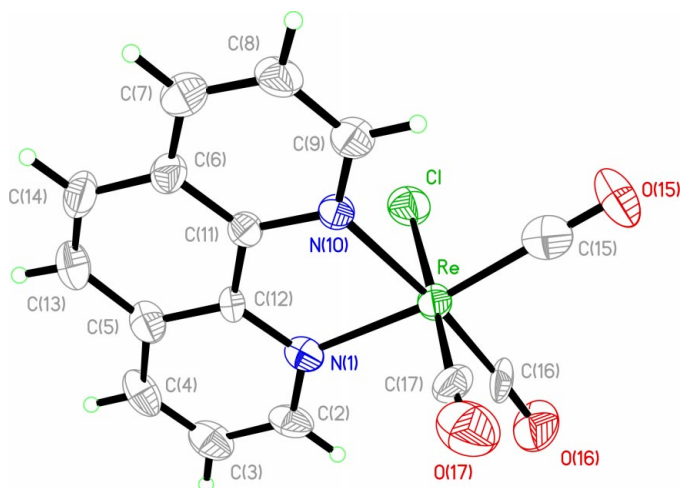
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**Comment**

Charge-transfer excited states of rhenium(I) diimine complexes result in properties which make these molecules useful as photosensitizers in photochemical and photoelectron transfer reactions (Luong *et al.*, 1978; Richter *et al.*, 1996; Stufkens & Vlcek, 1998), as well as *in situ* chemical probes (Lees, 1998; Tran *et al.*, 1997). The existence of a Frank–Condon-type barrier between close-lying metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) states for both the singlet states and for the triplet manifolds has been suggested (Striplin & Crosby, 1994; Striplin & Crosby, 2001); also the possibility of preferential loading of the triplet manifolds that is dependent on the nature of the singlet state to which the molecule is excited or of the singlet state to which the excited state initially deactivates through internal conversion (IC). The title compound, (I), is one molecule in a series of rhenium(I) complexes which have been synthesized to examine the validity of the barrier proposal.



The asymmetric unit is shown in Fig. 1. The Re—N distances are 2.181 (5) and 2.186 (5) Å, and the bidentate bite angle N—Re—N is 75.8 (2)°. The Cl—Re—N bond angles are 83.40 (12) and 85.43 (12)°, significantly less than expected for octahedral geometry. There is a noticeable *trans* influence



**Figure 1**  
A view of (I). Displacement ellipsoids are drawn at the 25% probability level.

induced by the  $\text{Cl}^-$  anion on the carbonyl  $\text{Re}-\text{C}$  distance. The  $\text{Re}-\text{C}17$  distance is *ca.* 0.05 Å longer than the  $\text{Re}-\text{C}15$  and  $\text{Re}-\text{C}16$  distances. The bidentate 1,10-phenanthroline deviates slightly from planarity, with a dihedral angle between its two heterocyclic rings of  $5.48(0.34)^\circ$ , and is folded away from the chloride anion. The  $\text{Re}(\text{I})$  atom lies 0.192 (3) Å from the least-squares plane of 1,10-phenanthroline (Fig. 2).

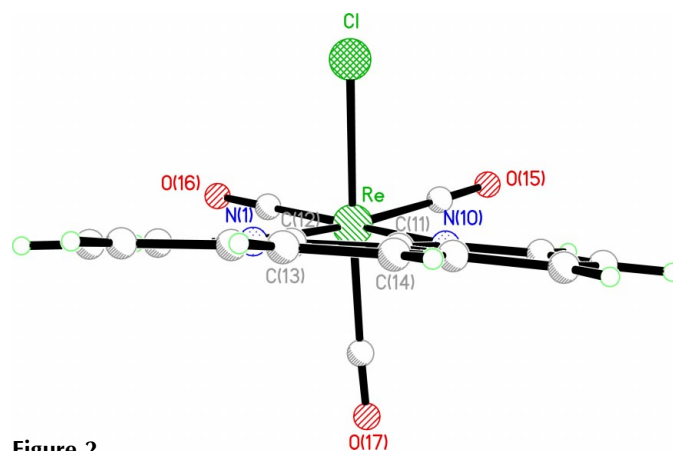
Some  $\text{C}-\text{H}\cdots\text{Cl}$  interactions exist (Neve & Crispini, 2001; Freytag *et al.*, 1999), also  $\text{C}-\text{H}\cdots\text{O}$  interactions, as shown in Fig. 3:  $\text{Cl}\cdots\text{C}2^{\text{i}}$  3.584 (6),  $\text{Cl}\cdots\text{C}3^{\text{ii}}$  3.704 (6),  $\text{O}15\cdots\text{C}9^{\text{iii}}$  3.498 (7),  $\text{O}16\cdots\text{C}7^{\text{iv}}$  3.393 (8),  $\text{O}16\cdots\text{C}14^{\text{v}}$  3.473,  $\text{O}17\cdots\text{C}7^{\text{vi}}$  3.460 (8),  $\text{O}17\cdots\text{C}9^{\text{vii}}$  3.378 (7) Å [symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $1-x, 1-y, -z$ ; (iii)  $-x, 2-y, 1-z$ ; (iv)  $1+x, 1+y, z$ ; (v)  $1+x, 1+y, z$ ; (vi)  $-x, 1-y, 1-z$ ; (vii)  $1+x, 1+y, z$ ]. These long H contacts with electronegative  $\text{Cl}^-$  and O may account for the folding in the 1,10-phenanthroline moiety. There are no stacking effects between adjacent 1,10-phenanthroline moieties; the closest atomic contact of 3.285 (11) Å is between C2 and  $\text{C}3^{\text{viii}}$  [symmetry code: (viii)  $1-x, 1-y, z$ ].

## Experimental

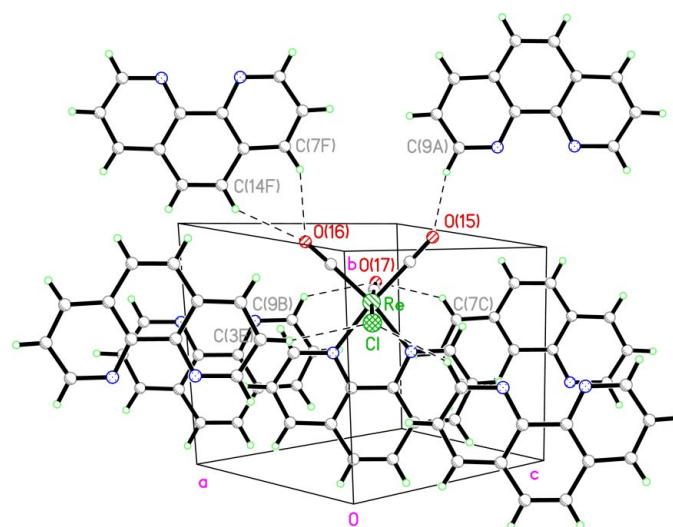
Rhenium pentacarbonyl chloride (0.1 mmol, 37 mg) and 1,10-phenanthroline (0.11 mmol, 20 mg) were refluxed in toluene for 1 h under  $\text{N}_2$ . The resulting yellow precipitate was collected by vacuum filtration and chromatographed on a column of silica gel (60–200 mesh), first with  $\text{CH}_2\text{Cl}_2$  to elute unreacted starting materials, and then with 5% methanol in  $\text{CH}_2\text{Cl}_2$  to elute the desired product. Slow evaporation of the solvent yielded the product as yellow crystals.

### Crystal data

$[\text{Re}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{CO})_3\text{Cl}]$	$Z = 2$
$M_r = 485.88$	$D_x = 2.262 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.4536(14) \text{ \AA}$	Cell parameters from 950 reflections
$b = 9.132(2) \text{ \AA}$	$\theta = 2.4\text{--}27.4^\circ$
$c = 12.841(3) \text{ \AA}$	$\mu = 8.72 \text{ mm}^{-1}$
$\alpha = 108.264(3)^\circ$	$T = 203(2) \text{ K}$
$\beta = 95.935(3)^\circ$	Plate, yellow
$\gamma = 91.440(3)^\circ$	$0.13 \times 0.08 \times 0.03 \text{ mm}$
$V = 713.5(3) \text{ \AA}^3$	



**Figure 2**  
Equatorial view of the 1,10-phenanthroline moiety in (I).



**Figure 3**  
Intermolecular hydrogen contacts involving  $\text{Cl}^-$  and carbonyl O atoms. Only one complete molecule of (I) is shown. Contacts to the 1,10-phenanthroline units of other molecules are represented by dashed lines.

### Data collection

Siemens SMART 1K CCD diffractometer	2509 independent reflections
$\omega$ scans	2286 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.397, T_{\text{max}} = 0.780$	$\theta_{\text{max}} = 25.0^\circ$
7351 measured reflections	$h = -7 \rightarrow 7$
	$k = -10 \rightarrow 10$
	$l = -15 \rightarrow 15$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2509 reflections	$\Delta\rho_{\text{max}} = 1.91 \text{ e \AA}^{-3}$
200 parameters	$\Delta\rho_{\text{min}} = -1.38 \text{ e \AA}^{-3}$

H atoms were placed geometrically and refined using a riding model, with  $U_{\text{iso}}$  values constrained to be  $1.2U_{\text{eq}}$  of the carrier atom. The largest residual electron density peak is  $1.91 \text{ e \AA}^{-3}$  and lies at  $1.06 \text{ \AA}$  from the Re atom.

Data collection: SMART (Bruker, 1997–98); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SHELXTL (Sheldrick,

1998); program(s) used to solve structure: *XS* in *SHELXTL*; program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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## References

- Bruker (1997–98). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
- Freytag, M., Jones, P. G., Ahrens, B. & Fischer, A. K. (1999). *New J. Chem.* **23**, 1137–1139.
- Lees, A. J. (1998). *Coord. Chem. Rev.* **177**, 3–35.
- Luong, J. C., Nadjo, L. & Wrighton, M. S. (1978). *J. Am. Chem. Soc.* **100**, 5790–5795.
- Neve, F. & Crispini, A. (2001). *Cryst. Growth Des.* **1**, 387–393.
- Richter, M. M., Debad, J. D., Striplin, D. R., Crosby, G. A. & Bard, A. J. (1996). *Anal. Chem.* **68**, 4370–4376.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1999). *SADABS*. Version 2.01. Bruker AXS Inc., Madison, Wisconsin, USA.
- Striplin, D. R. & Crosby, G. A. (1994). *Chem. Phys. Lett.* **221**, 426–430.
- Striplin, D. R. & Crosby, G. A. (2001). *Coord. Chem. Rev.* **211**, 163–175.
- Stufkens, D. J. & Vlcek, A. Jr (1998). *Coord. Chem. Rev.* **177**, 127–179.
- Tran, D., Bourassa, J. L. & Ford, P. (1997). *Inorg. Chem.* **36**, 439–442.