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# *fac*-Tricarbonyl[bis(2-pyridylmethyl) ether-*N*,*O*,*N'*]molybdenum(0)

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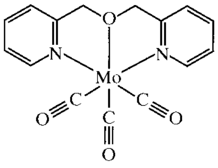
Reaction of bis(2-pyridylmethyl) ether with [$Mo(CO)_3(MeCN)_3$] in MeCN gives the title compound, [$Mo(C_{12}H_{12}N_2O)(CO)_3$], (I), as a yellow crystalline product. Compound (I) has been characterized by $^1$H NMR and IR spectroscopy, and single-crystal X-ray crystallography. In contrast with other examples of low-valent early transition metal complexes of ethers, the ether linkage of (I) appears relatively inert. Nevertheless, the weak donor property of the ether ligand is evidenced by a *trans* effect manifested as a short Mo—CO bond length for the carbonyl ligand *trans* to the ether ligand.

## Comment

Low-valent early transition metals (*e.g.* zero-valent group VI metals) generally prefer to be ligated by soft donors, preferably $\pi$-acids. Ethers are particularly poor ligands for such metals since they are generally weak Lewis bases, they bear hard donor atoms, and they are incapable of charge-balancing *via* back donation. These properties of ethers have been advantageous in the development of hemi-labile ligands (Chadwell *et al.*, 1996; Dunbar *et al.*, 1990, 1994; Mason *et al.*, 1991). In the present study, a relatively stable ether complex has been synthesized by employing the chelating ligand bis(2-pyridylmethyl) ether (bpme). In contrast to other metal–ether complexes that react with nitriles (Anderson & Kumar, 1984; Dunbar *et al.*, 1990; Lindner *et al.*, 1987), the title compound, (I), is synthesized in acetonitrile and its ether ligand shows no propensity for substitution by donor solvents.



(I)

The $^1$H NMR spectrum of (I) is comparable to that of the free bpme ligand, although the methylene groups of (I) are diastereotopic. At 300 MHz, the methylene region is second-order. The chemical shifts and coupling constants for the methylene groups of (I) that are reported in the *Experimental* section were derived from the second-order spectrum. The IR spectrum of (I) as a KBr pellet exhibits a sharp band at 1905 cm$^{-1}$ and a broad multi-featured band at 1800 cm$^{-1}$. These carbonyl vibrational frequencies are quite low. For comparison, the carbonyl stretching frequencies for [$Mo(CO)_3L$] where $L$ = $\eta^6$-benzene (Barbeau & Turcotte, 1976), 1,4,7-trithiacyclononane (ttcn) (Ashby *et al.*, 1986; Ashby & Lichtenberger, 1985) and 1,4,7-triazacyclononane (tacn) (Chaudhuri *et al.*, 1984) occur at 1985 and 1912, 1915 and 1783, and 1850 and 1730 cm$^{-1}$, respectively. Thus, the overall donor/acceptor ability of the bpme ligand is comparable to a soft $\sigma$-donor such as ttcn. Hard $\sigma$-donors such as tacn deliver considerably more electron density to the metal that is ultimately nullified in part by back-donation to the carbonyl ligands.

The Mo—N bond lengths of (I), 2.253 (2) and 2.265 (2) Å, are statistically equivalent to the average Mo—N distance of 2.266 (5) Å that has been found for 25 Mo(0)–pyridyl bonds (which range from 2.197 to 2.353 Å; Allen & Kennard, 1993). In contrast, the Mo—O bond length of (I), 2.290 (2) Å, is somewhat shorter than those reported previously for six Mo(0)–ether linkages (which range from 2.316 to 2.363 Å; Allen & Kennard, 1993). This shorter bond length may reflect a tighter binding of the O-donor of bpme. Interestingly, a *trans* effect is observed for (I) with respect to the Mo–carbonyl bond lengths. The Mo—CO that is *trans* to the ether ligand, 1.915 (3) Å, is statistically shorter than the two that are *trans* to pyridyl ligands, 1.939 (3) and 1.955 (3) Å. A similar *trans* effect is observed for other zero-valent group VI metal carbonyl complexes that bear ether ligands. Thus for [$Cr(CO)_5(THF)$], the Cr—(*trans*-CO) bond length is 1.812 (5) Å, whereas the average Cr—(*cis*-CO) bond length is 1.899 (11) Å (Schubert *et al.*, 1978). For a compound that is perhaps more closely related to (I), [$Mo(CO)_3\{(Ph_2CH_2P(CH_2CH_2OEt)_2\}_2$], one finds the Mo—CO bond lengths for the CO ligands that are *trans* to phosphine ligands, 1.964 (4) and 1.968 (4) Å, are longer than that for the CO that is *trans* to an ether ligand, 1.914 (4) Å (Chadwell *et al.*, 1996). A similar situation is observed for a related W compound where two 1.98 (1) Å bond lengths are observed for CO ligands *trans* to phosphine donors and 1.91 (1) Å for a CO ligand that is *trans*

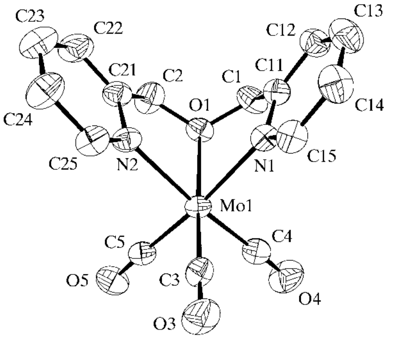


**Figure 1**
The molecular structure and labeling scheme of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

to an ether donor (Mason *et al.*, 1991). The crystal structure of $[Mo(CO)_4P\{C_6H_2(OMe)_3\}_3]$ illustrates nicely the comparative effects of CO, $PR_3$ and $OR_2$ on metal–carbonyl bond lengths (Dunbar *et al.*, 1994). Since ether ligands are ineffectual $\pi$-donors, the short $M-CO$ bond lengths for the carbonyl ligands *trans* to ether ligands may be attributed to a weak M—O $\sigma$ bond.

## Experimental

Preparation of bis(2-pyridylmethyl) ether (bpme): to dry THF (20 ml) was added NaH (0.6 g of a 60 wt% suspension in oil, 15 mmol) and 2-pyridylcarbinol (1.5 ml, 1.7 g, 15 mmol). After refluxing for 2 h, the solution was cooled to room temperature and 2-pyridylmethyl-*p*-toluenesulfonate (4.0 g, 15 mmol; preparation details deposited) was added. The mixture was refluxed for 2 d. After cooling to room temperature, water (50 ml) was added and the product was extracted with ether (2 × 50 ml). The organic layer was dried with $CaCl_2$, and the ether was removed on a rotary evaporator to give the crude product as a yellow oil. The crude oil was dissolved in 5% aqueous HCl (100 ml) and an organic impurity was removed by extraction with ether (2 × 50 ml). The aqueous layer was neutralized with aqueous NaOH. The product was extracted with ether (2 × 50 ml), the organic layer was dried with $CaCl_2$, and the ether was removed on a rotary evaporator to give the product as a colorless oil (19% yield). $^1$H NMR ($CDCl_3$, 293 K, 300 MHz): $\delta$ 8.55 (*d*, 1H, $J$ = 4 Hz), 7.70 (*td*, 1H, $J$ = 8, $J'$ = 2 Hz), 7.51 (*d*, 1H, $J$ = 8 Hz), 7.22 (*dd*, 1H, $J$ = 5, $J'$ = 7 Hz), 4.77 (*s*, 2H) p.p.m.

Preparation of tricarbonyl[bis(2-pyridylmethyl) ether-*N*,*O*,*N*′]-molybdenum(0), (I): acetonitrile (30 ml) and $Mo(CO)_6$ (309 mg, 1.17 mmol) were added to a Schlenk flask. The resulting solution was freeze-pump-thawed and the flask was placed in a 353 K oil bath. After 1 h, the flask was removed from the oil bath, the solution was frozen, and the CO that had evolved was pumped away. The flask was returned to the oil bath and the process of removing the CO repeated twice more. The bpme ligand (250 mg, 1.25 mmol) was added, the solution freeze-pump-thawed, and the sealed flask returned to the oil bath for 1 h. The resulting yellow precipitate was collected on a Schlenk frit, washed with dry pentane and dried under vacuum (47% yield). $^1$H NMR (acetone-$d_6$, 293 K, 300 MHz): $\delta$ 8.91 (*d*, 1H, $J$ = 5 Hz), 7.79 (*td*, 1H, $J$ = 8, $J'$ = 2 Hz), 7.38 (*d*, 1H, $J$ = 8 Hz), 7.30 (*t*, 1H, $J$ = 8 Hz), 5.52, 5.15 (*AB*, 2H, $J$ = 16 Hz) p.p.m.; IR (KBr): 1905 (*s*), 1800 (*br*) cm$^{-1}$. Analysis calculated for $C_{15}H_{12}MoN_2O_4$ (fw = 548.20): C 32.86, H 2.21%; found: C 33.41, H 2.96%.

### Crystal data

$[Mo(C_{12}H_{12}N_2O)(CO)_3]$
$M_r = 380.21$
Orthorhombic, *Pbca*
$a = 13.864\ (1)$ Å
$b = 13.339\ (1)$ Å
$c = 16.464\ (1)$ Å
$V = 3044.7\ (4)$ Å$^3$
$Z = 8$
$D_x = 1.659$ Mg m$^{-3}$

$D_m$ not measured
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 10.61–24.96°$
$\mu = 0.880$ mm$^{-1}$
$T = 198\ (2)$ K
Plate, yellow
0.36 × 0.28 × 0.24 mm

### Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
3376 measured reflections
2660 independent reflections
2196 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 24.99°$

$h = -1 \rightarrow 16$
$k = -1 \rightarrow 15$
$l = -19 \rightarrow 1$
3 standard reflections every 97 reflections
intensity decay: 6.69%

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.076$
2655 reflections
247 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.7814P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.010$
$\Delta\rho_{\rm max} = 0.398$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.363$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Mo1—C3 | 1.915 (3) | Mo1—N1 | 2.253 (2) |
| Mo1—C5 | 1.939 (3) | Mo1—N2 | 2.265 (2) |
| Mo1—C4 | 1.955 (3) | Mo1—O1 | 2.290 (2) |
| | | | |
| C3—Mo1—C5 | 87.49 (11) | C4—Mo1—N2 | 171.76 (10) |
| C3—Mo1—C4 | 87.33 (12) | N1—Mo1—N2 | 79.88 (8) |
| C5—Mo1—C4 | 85.47 (11) | C3—Mo1—O1 | 169.56 (9) |
| C3—Mo1—N1 | 98.01 (10) | C5—Mo1—O1 | 101.32 (9) |
| C5—Mo1—N1 | 173.59 (9) | C4—Mo1—O1 | 98.84 (10) |
| C4—Mo1—N1 | 98.02 (10) | N1—Mo1—O1 | 72.88 (7) |
| C3—Mo1—N2 | 100.83 (10) | N2—Mo1—O1 | 72.92 (8) |
| C5—Mo1—N2 | 95.92 (10) | | |

Based on systematic absences of 0*kl*, $k = 2n + 1$, *h*0*l*, $l = 2n + 1$, and *hk*0, $h = 2n + 1$ the space group was uniquely determined to be *Pbca* (#61). The H atoms were located in the difference map and refined isotropically; C–H distances are in the range 0.90 (3)–1.05 (4) Å. Absorption correction was not applied since it was judged to be insignificant.

Data collection: *XSCANS* (Siemens, 1994*a*); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1090). Services for accessing these data are described at the back of the journal.

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