Organometallics **1993**, *12*, 1481–1483

$Ni(CO)_4$ and $Fe(CO)_5$: Molecular Structures in the Solid State

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Received September 21, 1992

Summary: Precise, low-temperature crystal structures of the archetypal mononuclear metal carbonyls $Ni(CO)_4$ *and* $Fe(CO)_5$ *are reported.* $Ni(CO)_4$ *is tetrahedral with Ni–C = 1.817(2) Å and C–O = 1.127(3) Å.* $Fe(CO)_5$ *is slightly distorted (in an anti-Berry pseudorotation sense) from ideal trigonal-bipyramidal geometry with mean axial Fe–C = 1.811(2) Å and C–O 1.117(2) Å and mean equatorial Fe–C = 1.803(2) Å and C–O = 1.133(3) Å. Crystal data at 198 K:* $Ni(CO)_4$*, space group* $Pa\bar{3}$*, a = 10.832(5) Å, Z = 8, 937 unique reflections out of 3160 measured reflections,* $R(F) = 0.042$, $R_w(F^2) = 0.090$; $Fe(CO)_5$*, space group C2/c, a = 11.740(2) Å, b = 6.806(1) Å, c = 9.341(3) Å, β = 107.59(1)°, Z = 4, 823 unique reflections out of 954 measured reflections,* $R(F) = 0.019$, $R_w(F^2) = 0.057$.

The solid-state structures of nickel tetracarbonyl[1] and iron pentacarbonyl[2] are known with limited precision (and accuracy?) in spite of their importance as prototypical metal carbonyl complexes and as precursors of many thousands of organometallic species. In part the lack of precise studies compared with those carried out on, for example, $Cr(CO)_6$,[3] is a consequence of the low melting points, high vapor pressures, and high toxicity of both complexes, particularly in the case of $Ni(CO)_4$.[4] In the course of our studies[5] on the fine structural details, molecular packing, and solid-state dynamics of organometallic species we felt that it was high time that the structures of these two molecules were redetermined by up-to-date methods. Our objectives were to provide precise dimensions for these archetypal species for use in calibration of quantum-mechanical treatments of metal carbonyls, of molecular modeling procedures, and atom–atom potential models of their crystal structures.[6] In addition, precise structure analyses are invaluable for detailed evaluation of dynamic solid-state processes in these systems[7] and for comparison with the results of structure determinations in other phases, e.g. gas-phase electron diffraction.[8]

Results and Discussion

Single-crystal X-ray diffraction intensities for each compound were measured by counter methods at two temperatures (198 and 228 K) on single crystals grown directly on the diffractometer by repeated cycles of partial melting and refreezing of the pure liquids contained in 0.3-mm thin-walled glass capillaries. The available atomic coordinates of $Ni(CO)_4$ and $Fe(CO)_5$ were used as starting points for refinement of data. In the following only the results of the refinements[9] against the full lower temperature data sets will be discussed. High-order refinements, thermal motion analysis, and a detailed analysis of the molecular and crystal structures will be the subject of a future full paper. Crystal data and details of measurements for the two data collections at 198 K are reported in Table I. Fractional atomic coordinates and relevant bond distances and angles are reported in Tables II and III, respectively.

Within the context of this note we wish to summarize only the main structural observations.

(i) Space group determination and structural refinement give results that are consistent with the previous reports; we unequivocally confirm that the correct space group choice for $Fe(CO)_5$ is *C*2/*c*.

(ii) In the solid state $Ni(CO)_4$ is tetrahedral within experimental uncertainties; the molecule lies on a crystallographic 3-fold axis (Figure 1).

(iii) Ni–C and C–O distances show, however, substantial differences (in light of the current precision) from the previously reported values: Ni–C and C–O bond lengths for the unique C(1)O(1) carbonyl are 1.819(3) and 1.125(3) Å, while those for the general position carbonyl C(2)-O(2) are 1.815(2) and 1.128(3) Å with Ni–C–O = 179.7(1)°. These values are to be compared with 1.84(3) and 1.15(3) Å in the early X-ray single-crystal study[1] and 1.835(2) and 1.139(2) Å by gas-phase electron diffraction[8a,10] (r_a values).

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(9) (a) Complex, neutral atom scattering factors taken from: *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland, 1992; Vol. C. (b) Sheldrick, G. M. SHELXL92; University of Gottingen, Gottingen, Germany, 1992.

0276-7333/93/2312-1481$04.00/0

Table I. Crystal Data and Details of Measurements for Ni(CO)$_4$ and Fe(CO)$_5$

	Ni(CO)$_4$	Fe(CO)$_5$
formula	C_4NiO_4	C_5FeO_5
space group	$Pa\bar{3}$	$C2/c$
a, Å	10.832(5)	11.740(2)
b, Å		6.806(1)
c, Å		9.341(3)
β, deg		107.59(1)
V, Å^3	1270.9	711.5
Z	8	4
temp, K	198	198
λ(Mo Kα), Å	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	2.99	2.09
transmission coeff^a	0.72–1.00	0.86–1.00
scan mode	$\omega/2\theta$	$\omega/2\theta$
2θ limits, deg	70	60
no. of rflns measd	3160	954
R_{int}	0.033	0.013
no. of unique rflns	937	823
no. of unique rflns ($F^2 > 2\sigma(F^2)$)^a	604	752
no. of variables	28	52
$R_w(F^2)^b$	0.090	0.057
R_F	0.042	0.019
GOF	1.506	1.483

[a] Intensity data were corrected for absorption by azimuthal scanning at 10° steps (ψ scan, $\chi > 80°$) of seven and three reflections for Ni(CO)$_4$ and Fe(CO)$_5$, respectively. [b] For least-squares refinements (against unique F^2 values) the SHELXL92 program was used.[9b]

Table II. Atomic Coordinates for Ni(CO)$_4$ and Fe(CO)$_5$

atom	x	y	z
		Ni(CO)$_4$	
Ni	0.12184(2)	0.12184(2)	0.12184(2)
C1	0.21878(15)	0.21878(15)	0.21878(15)
O1	0.27872(12)	0.27872(12)	0.27872(12)
C2	0.0231(2)	0.02757(15)	0.2190(2)
O2	−0.03870(14)	−0.03102(13)	0.27895(15)
		Fe(CO)$_5$	
Fe1	0.0000	0.16650(4)	0.2500
C1	0.08312(13)	0.3035(2)	0.4136(2)
C2	0.12939(15)	0.1640(2)	0.1828(2)
C3	0.0000	−0.0981(4)	0.2500
O1	0.13541(12)	0.3912(3)	0.5158(2)
O2	0.20922(13)	0.1609(2)	0.1413(2)
O3	0.0000	−0.2639(3)	0.2500

Table III. Bond Lengths (Å) and Angles (deg)

	Ni(CO)$_4$		
Ni–C2	1.815(2)	C1–O1	1.125(3)
Ni–C1	1.819(3)	C2–O2	1.128(2)
C2–Ni–C2a	109.65(6)	O1–C1–Ni	180.0
C2–Ni–C1	109.29(6)	O2–C2–Ni	179.66(15)
	Fe(CO)$_5$		
Fe1–C3	1.801(3)	C1–O1	1.136(2)
Fe1–C1	1.804(2)	C2–O2	1.117(2)
Fe1–C2	1.811(2)	C3–O3	1.128(4)
C3–Fe1–C1	121.11(5)	C2–Fe1–C2a	178.94(10)
C1–Fe1–C1a	117.78(10)	O1–C1–Fe1	179.4(2)
C3–Fe1–C2	89.47(5)	O2–C2–Fe1	179.43(15)
C1–Fe1–C2	90.38(7)	O3–C3–Fe1	180.0

(iv) Fe(CO)$_5$ possesses the well-known trigonal-bipyramidal structure, with the crystallographic 2-fold axis passing through C(3)O(3) and the Fe atom (Figure 2).

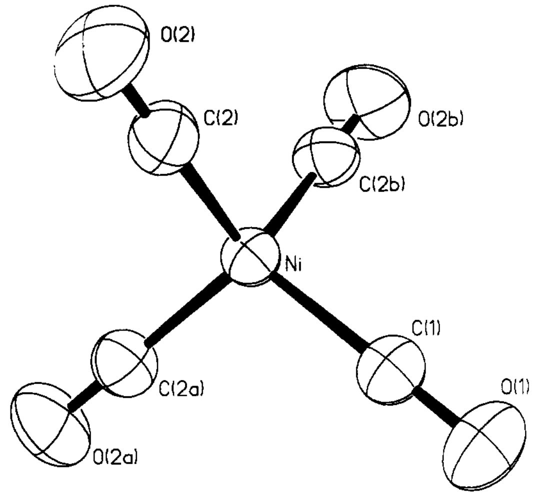

Figure 1. Displacement ellipsoid plot (50%) of the molecular structure of Ni(CO)$_4$. The crystallographic 3-fold axis passes through atoms Ni, C(1), and O(1).

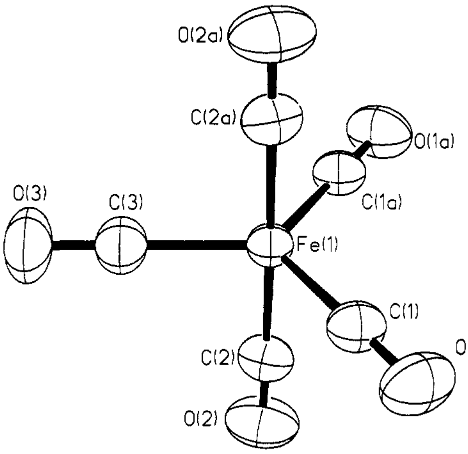

Figure 2. Displacement ellipsoid plot (50%) of the molecular structure of Fe(CO)$_5$. The crystallographic 2-fold axis passes through atoms Fe(1), C(3), and O(3).

(v) The equatorial carbonyl ligands C(1)O(1) and C(3)O(3) show *slightly* shorter Fe–C and longer C–O bond lengths (1.804(2), 1.801(3) Å; 1.136(2), 1.128(4) Å; average Fe–C–O = 179.4(2)°) than does the axial ligand C(2)O(2) (1.811(2), 117(2) Å). In the earlier $C2/c$ refinement carried out by Donohue and Caron,[2b] Fe–C distances were found to range from 1.76(3) to 1.81(3) Å (average 1.79(4) Å), while C–O ranged from 1.10(4) to 1.14(2) (average 1.12(2) Å). The magnitude of the Fe–C axial vs equatorial bond length distortion (0.44%) is notably less than in analogous p-block trigonal-bipyramidal species (e.g. in PF$_5$ P–F$_{ax}$ = 1.577 Å and P–F$_{eq}$ = 1.534 Å; i.e. distortion 2.8%, by gas-phase electron diffraction).[11] Interestingly, in the most recent gas-phase electron diffraction study[8b,10] the average equatorial Fe–C distance was reported to be *longer* than the axial value (1.827(3) vs 1.807(3) Å) while the C–O distances were indistinguishable (mean C–O = 1.152(3) Å).

(vi) There is a small angular distortion of the trigonal bipyramid in crystalline Fe(CO)$_5$ with the axial ligands closing on the unique carbonyl (C(1)–Fe–C(2) = 89.47(5)°, C(2)–Fe–C(2a) = 178.94(10)°), two equatorial angles opened from their ideal values (C(3)–Fe–C(1) = 121.11(5)°), and the third slightly closed (C(1)–Fe–C(1a) = 117.8(1)°). This distortion is of an anti-Berry pseudorotation

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(10) We note that the comparison of geometric parameters derived from crystallographic and gas-phase studies is fraught with difficulties. In particular, corrections must be applied to both sets of results. These corrections are nontrivial, especially for near-linear but flexible M–C–O units.

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type, i.e. in the direction *away* from a square-based pyramidal geometry in which C(1)–Fe–C(2) = C(1)–Fe–C(3) = *ca.* 105°.

Acknowledgment. This research was supported by the Ministero della Università e della Ricerca Scientifica e Tecnologica (Italy). A.G.O. thanks the Ciba-Geigy Foundation for the award of a Senior Research Fellowship and Prof. D. Braga and his colleagues at the Dipartimento di Chimica "G. Ciamician", Università di Bologna, for their hospitality during a sabbatical stay in Bologna. We thank Prof. G. Longoni for invaluable assistance in sample preparation.

Supplementary Material Available: A table of anisotropic displacement parameters (1 page). Ordering information is given on any current masthead page.

OM920577S