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Journal of Organometallic Chemistry 612 (2000) 96–105

Journal of Organo metallic Chemistry

Transition metal complexes of 2,2,2-trifluoroethyl isocyanide and 1H,1H-perfluorooctyl isocyanide

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Received 26 April 2000; accepted 20 June 2000

Abstract

1H,1H-Perfluorooctyl isocyanide (**2**) has been synthesized in two steps. The mononuclear complexes $(CO)_5Cr(CN–CH_2–R)$ (**3**) (**a**, R = CF_3; **b**, R = C_7F_{15}), *fac*-$(CO)_3M(CN–CH_2–R)_3$ (**4**) (**a**, M = Mo, R = CF_3; **b**, M = W, R = CF_3; **c**, M = W, R = C_7F_{15}), $Cp^*Mn(CO)_2(CN–CH_2–CF_3)$ (**5**), $Cl–Au–CN–CH_2–CF_3$ (**6**), have been prepared and characterized by spectroscopic methods. To study the tendency of $F_3C–CH_2–NC$ to act as a bridging ligand $Cp^*_2M_2(CO)_2(\mu_2\text{-}\eta^2\text{-}CN–CH_2–CF_3)$ (**7**) and $[Cp^*M(CO)_2(CN–CH_2–CF_3)]_2$ (**8**) (**a**, M = Mo; **b**, M = W) have been synthesized. The crystal and molecular structures of **4b**, **6** and **8a** have been elucidated by X-ray crystallography. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal complexes; Carbonyl ligands; Isocyanide ligands

1. Introduction

Isocyanides, R–NC, are extremely versatile ligands in transition metal chemistry as the selection of the organic substituent R allows to adjust the σ donor and π acceptor abilities of the ligand [1–3]. Whereas in general alkyl isocyanides, like methyl isocyanide, are good σ donor ligands the π acceptor ability increases when electron withdrawing groups are attached to the nitrogen atom [1]. As a consequence the π acceptor σ donor ratio increases with the number of fluorine atoms at the α carbon atom of substituted methyl isocyanides [4–6]. Trifluoromethyl isocyanide is one of the strongest π acceptor ligands known thus far [1,4,5]. However, α fluorinated isocyanides can be prepared only by difficult synthetic routes. The extremely unstable trifluoromethyl isocyanide which decomposes in condensed phase even at −78°C [7] is the only α fluorinated isocyanide which has been studied in detail [1]. Pentafluoroethyl isocyanide and heptafluoropropyl isocyanide were prepared recently by Shreeve et al. [8] but their coordination chemistry was not studied. Others like fluoromethyl isocyanide [6], difluoromethyl isocyanide [6,9], 1,2-dichloro-trifluoroethyl isocyanide [10], trifluorovinyl isocyanide [10], nonafluorobutyl isocyanide [11] or hexafluoro-1,2-diisocyanocyclobutane [12] were prepared by organometallic pathways stabilized at a pentacarbonyl chromium fragment. However, the generation of the isocyanide by flash vacuum pyrolysis was only possible for a few exceptions like trifluorovinyl isocyanide [10] and difluoromethyl isocyanide [9]. As 1H,1H-perfluoroamines are stable commercially available materials one can expect that the corresponding isocyanides can be synthesized by conventional isocyanide synthetic methods like the Ugi synthesis [13]. 2,2,2-Trifluoroethyl isocyanide was first prepared by Sergev et al. [14] and a few transition metal complexes were studied by Simonneaux et al. [15].

In continuation of our work on the fluorination effects on isocyanides we have started to study the coordination chemistry of 2,2,2-trifluoroethyl isocyanide. As highly fluorinated isocyanide ligands might be suitable for the use in the fluorous biphase system [16–18] we got interest in 1H,1H-perfluorooctyl isocyanide. Herein we report on our results in this area.

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PII: S0022-328X(00)00427-7

2. Results and discussion

2.1. 1H,1H-perfluorooctyl isocyanide and 2,2,2-trifluoroethyl isocyanide

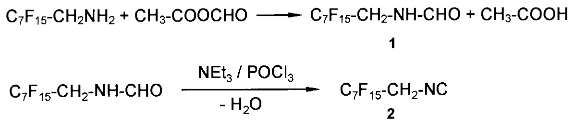
Like 2,2,2-trifluoroethyl isocyanide [14,15] 1H,1H-perfluorooctyl isocyanide is prepared in two steps starting with commercially available 1H,1H-perfluorooctyl amine (Scheme 1).

First 1H,1H-perfluorooctyl amine is converted into the formamide **1** by reaction with formylacetate in high yield. Dehydratisation of the formamide with phosphoryl chloride in the presence of triethyl amine at − 25°C yields the isocyanide **2** which was purified by fractional condensation. The characterization of **1** and **2** is based on spectroscopic methods. The ^{1}H-NMR spectrum of **1** consists of three signals at 3.99 (td, CH_2, $^3J_{H-F} = 8$, $^3J_{H-H} = 6$ Hz), 5.78 (s, br, NH) and 8.26 (s, CHO) ppm. Its ^{19}F-NMR spectrum exhibits one signal for the CF_3-group at − 79.5 ppm and six multiplets between − 116.8 and − 124.8 ppm for the CF_2 groups. A complete assignment of ^{19}F- and ^{13}C-NMR spectra of **2** is based on ^{19}F-^{19}F-COSY and ^{19}F-^{13}C-HMQC spectra. The obtained data are summarized in Table 1. The ^{13}C resonance of the isocyanide carbon is observed at 168.5 ppm which is a value typical for isocyanides. The NC vibration gives raise to an intense band in the IR spectrum at 2169 cm^{-1}.

The yield of 2,2,2-trifluoroethyl isocyanide is easily increased to 81.5% by a slightly modified work up procedure by fractional condensation to avoid thermal decomposition of the thermally unstable isocyanide. The spectroscopic data are in good agreement with the structure and published values. The results of low temperature crystal structure determination of 2,2,2-trifluoroethyl isocyanide were published recently [19].

2.2. Mononuclear complexes of 2,2,2-trifluoroethyl isocyanide and 1H,1H-perfluorooctyl isocyanide

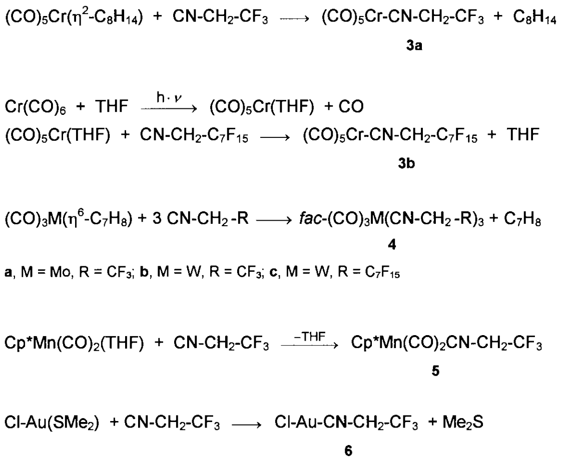
The synthesis of mononuclear complexes of 2,2,2-trifluoroethyl isocyanide and 1H,1H-perfluorooctyl isocyanide from labile metal complexes is straightforward (Scheme 2).



$$C_7F_{15}\text{-}CH_2NH_2 + CH_3\text{-}COOCHO \longrightarrow \underset{1}{C_7F_{15}\text{-}CH_2\text{-}NH\text{-}CHO} + CH_3\text{-}COOH$$

$$C_7F_{15}\text{-}CH_2\text{-}NH\text{-}CHO \xrightarrow[-H_2O]{NEt_3 / POCl_3} \underset{2}{C_7F_{15}\text{-}CH_2\text{-}NC}$$

Scheme 1.



$$(CO)_5Cr(\eta^2\text{-}C_8H_{14}) + CN\text{-}CH_2\text{-}CF_3 \longrightarrow \underset{3a}{(CO)_5Cr\text{-}CN\text{-}CH_2\text{-}CF_3} + C_8H_{14}$$

$$Cr(CO)_6 + THF \xrightarrow{h\cdot\nu} (CO)_5Cr(THF) + CO$$

$$(CO)_5Cr(THF) + CN\text{-}CH_2\text{-}C_7F_{15} \longrightarrow \underset{3b}{(CO)_5Cr\text{-}CN\text{-}CH_2\text{-}C_7F_{15}} + THF$$

$$(CO)_3M(\eta^6\text{-}C_7H_8) + 3\ CN\text{-}CH_2\text{-}R \longrightarrow \underset{4}{fac\text{-}(CO)_3M(CN\text{-}CH_2\text{-}R)_3} + C_7H_8$$

a, M = Mo, R = CF_3; **b**, M = W, R = CF_3; **c**, M = W, R = C_7F_{15}

$$Cp^*Mn(CO)_2(THF) + CN\text{-}CH_2\text{-}CF_3 \xrightarrow{-THF} \underset{5}{Cp^*Mn(CO)_2CN\text{-}CH_2\text{-}CF_3}$$

$$Cl\text{-}Au(SMe_2) + CN\text{-}CH_2\text{-}CF_3 \longrightarrow \underset{6}{Cl\text{-}Au\text{-}CN\text{-}CH_2\text{-}CF_3} + Me_2S$$

Scheme 2.

However, in contrast to trifluoromethyl isocyanide [20], no ligand substitution is observed in the reaction of dicarbonyl(pentamethylcyclopentadienyl)cobalt with 2,2,2-trifluoroethyl isocyanide. All compounds were fully characterized by spectroscopic methods. Additionally the structures of *fac*-tricarbonyltris(2,2,2-trifluoroethyl isocyanide)tungsten (**4b**) and chloro(2,2,2-trifluoroethyl isocyanide)gold (**6**) were studied by single crystal X-ray diffraction.

A comparison of the ^{13}C-NMR data of pentacarbonyl(2,2,2-trifluoroethyl isocyanide)-chromium (**3a**) and pentacarbonyl(1H,1H-perfluorooctyl isocyanide)chromium (**3b**) with the data of known complexes of the type $(CO)_5Cr(L)$ allows us an estimation of the π acceptor and σ donor behavior of these isocyanide ligands. The difference in the chemical shift values of the *cis* and *trans* carbonyl ligand are strongly influenced by the electronic properties of the ligand L. The data of several pentacarbonylchromium complexes are summarized in Table 2. In most cases $\delta_{cis} - \delta_{trans}$ possesses a negative value in other words the signal of the *trans* carbonyl ligand is observed at lower field (higher frequency) than the one of the *cis* carbonyl ligands. Exceptions from this 'rule' have been found only for the very strong π acceptor ligands CS, CSe [21], CN–CN [22], $F_2ClC\text{–}CFCl\text{–}NC$ [10] and $F_3C\text{–}NC$ [4].

The differences $\delta_{cis} - \delta_{trans}$ of − 1.6 and − 1.5 for **3a** and **3b** are comparable with the values obtained for the

Table 1
NMR data of 1H,1H-perfluorooctyl isocyanide

	CF_3	ζ-CF_2	ε-CF_2	δ-CF_2	γ-CF_2	β-CF_2	α-CF_2	CH_2	NC
^{1}H								4.08	
^{19}F	−79.6	−121.5	−120.8	−125.0	−121.6	−120.6	−115.8		
^{13}C	117.3	110.8	110.8	108.5	110.3	110.9	113.2	42.3	165.8

Table 2
Chemical shift values of the carbonyl ligands of complexes (CO)CrL

L	$\delta(CO_{cis})$	$\delta(CO_{trans})$	$\Delta\delta = \delta_{cis} - \delta_{trans}$	Literature
CF_3NC	211.7	211.5	0.2	[4]
CS	211.4	211.4	0.0	[21]
CNCN	212.6	212.6	0.0	[22]
$CF_2Cl–CFClNC$	212.0	212.0	0.0	[10]
$CHF_2–NC$	213.1	213.7	−0.6	[6]
$Cl_2HC–CCl_2–NC$	212.7	213.5	−0.8	[11]
$Cl_3C–NC$	212.6	213.5	−0.9	[11]
$ClH_2C–CCl_2–NC$	212.9	214.1	−1.2	[11]
$Cl_2HC–NC$	212.9	214.1	−1.2	[11]
$F_2C{=}CF–NC$	213.0	214.2	−1.2	[6]
$F_5C_6–NC$	213.3	214.6	−1.3	[23]
$CHF{=}CF–NC$	213.0	214.3	−1.3	[24]
$NC–CH_2–NC$	214.3	215.8	−1.5	[25]
$CN–CH_2–NC$	214.1	215.6	−1.5	[26]
$CH_2F–NC$	214.5	216.0	−1.5	[10]
$CF_3(CF_2)_6CH_2–NC$	213.9	215.4	−1.5	This work
$CF_3–CH_2–NC$	213.9	215.5	−1.6	This work
CO	212.1	212.1	0.0	[44]

Table 3
IR data and CO force constants in $Cp^*Mn(CO)_2L$ and *fac*-$(CO)_3W(CN–R)_3$

Compound	$\nu(CO)$ (cm^{-1})	$k(CO)$ ($N\ cm^{-1}$)	Literature
$Cp^*Mn(CO)_2(CNCH_3)$	1940, 1893	14.83	[5]
$Cp^*Mn(CO)_3$	2010, 1918	15.35	[5]
$Cp^*Mn(CO)_2(CN–CH_2–CF_3)$	1998, 1924	15.53	This work
$Cp^*Mn(CO)_2(CN–C_6F_5)$	2004, 1927	15.61	[27]
$Cp^*Mn(CO)_2(CN–CF_3)$	2007, 1945	15.77	[5]
fac-$(CO)_3W(CN\text{-}t\text{-}Bu)_3$	1932, 1856	14.30	[28]
fac-$(CO)_3W(CN–CH_2–CN)_3$	1945, 1893	14.74	[25]
fac-$(CO)_3W(CN–CH_2–CF_3)_3$	1952, 1902	14.87	This work

fluoromethyl isocyanide and isocyanoacetonitrile ligand.

An independent estimation of the ligand properties of 2,2,2-trifluorethyl isocyanide can be made from the vibrational spectroscopic data of the half sandwich complexes $Cp^*Mn(CO)_2L$ and *fac*-$(CO)_3W(CN–R)_3$ (Table 3), respectively.

The CO force constant can be easily calculated by a method described by Cotton and Kraihanzel [29]. A large CO force constant is due to a low electron density in the π* orbitals of the carbonyl ligands caused by a strong π accepting ligand in competition with the carbonyl ligand. Vice versa a small CO force constant indicates a weak π accepting ligand. A quantitative result can not be obtained due to the fact that this approximation ignores coupling between the CO and CN stretching modes. However, a similar trend can be observed as in the ^{13}C-NMR studies of the pentacarbonyl chromium complexes indicating a π acceptor/σ donor ratio comparable to that of isocyanoacetonitrile.

Although there is no ambiguity in the facial orientation of the ligands in the compounds **4** both from IR and NMR data we expected to get more detailed information from a X-ray crystal structure analysis of **4a**. Compound **4a** crystallizes monoclinic $P2_1/m$ with half a molecule in the asymmetric unit. A Pluto plot demonstrating the crystallographic C_s symmetry of the molecule is depicted in Fig. 1. As expected carbon metal distances to the carbonyl ligands are about 0.1 Å shorter than those to the isocyanide ligands. As there exist no tricarbonyl(triisocyanide)molybdenum complex structurally characterized by X-ray diffraction a comparison of the structural data can be made only with analogous tungsten complexes. The difference in the metal–carbon distances is slightly larger than that observed in the structure determination of $W(CO)_3(CN–C_6F_5)_3$ complex with a meridional structure [23]. All other $W(CO)_3(CNR)_3$ complexes which have been characterized crystallographically exist as the facial isomer, however, this geometry might be forced by the tripodal nature of the isocyanide ligand [30–32] (Table 5).

The molecular structure and crystal packing of $ClAu(CN–CH_2–CF_3)$ (**6**) is shown in Fig. 2 in two views. $ClAu(CN–CH_2–CF_3)$ crystallises monoclinic. Systematic extinction does not allow an unambiguous determination of the spacegroup giving the choice between $P2_1$ (acentric) and $P2_1/m$ (centric). The structure can be solved and refined in the acentric spacegroup $P2_1$. However, an additional symmetry check using PLATON [33] found a crystallographic mirror plane as

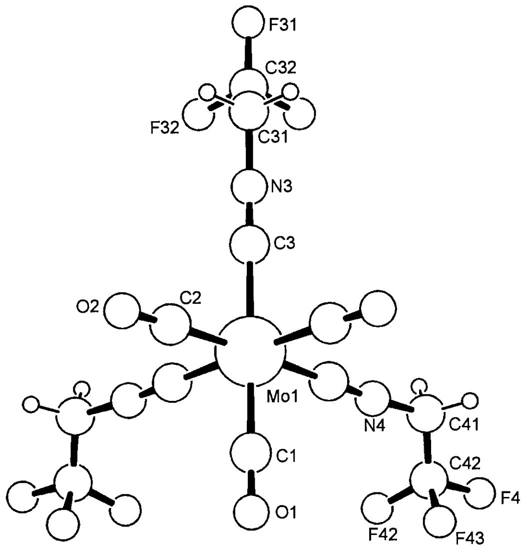


Fig. 1. Molecular structure (PLUTO [31]) of *fac*-$(CO)_3Mo(CN–CH_2–CF_3)_3$ (**4a**).

Table 5
Selected bond lengths (Å) and angles (°) for *fac*-tricarbonyltris(2,2,2-trifluoroethyl isocyanide)molybdenum (**4a**)

Mo(1)–C(1)	1.994(12)
Mo(1)–C(2)	2.007(9)
Mo(1)–C(4)	2.106(7)
Mo(1)–C(3)	2.134(10)
C(3)–N(3)	1.147(13)
C(4)–N(4)	1.156(9)
C(31)–N(3)	1.448(15)
C(41)–N(4)	1.420(11)
C(3)–N(3)–C(31)	168.1(12)
C(4)–N(4)–C(41)	175.7(9)

additional symmetry element. Thus the structure was solved and refined in the centro symmetric space group $P2_1/m$.

Important bond lengths and angles are summarized in Table 6. The individual molecules are rod-like with crystallographic C_s symmetry. The Cl–Au–C angle is close to 180° [178.4(6)°], as well as the Au–C–N angle of 179(2.0) and the C–N–C angle of 178(2)°. The short Au–C distance of 1.95(2) Å compared to $(Ph_3P)AuCH_3$ [Au–C 2.124(3) Å] [34] is presumably due to the sp hybridization of the isocyanide carbon atom and not reflecting a large amount of backbonding. The crystal packing (normal to 010 and 100) is shown in Fig. 2 is similar to that of $ClAu(CNCH_3)$ described by Schmidbaur et al. [35]. Shortest intermolecular gold contacts of 3.47 Å are observed orientated in an antiparallel fashion compared to 3.637(1) for $ClAu(CNCH_3)$ and 3.463(1) Å for $ClAu(CN–C_6H_5)$ [35].

Table 6
Selected bond lengths (Å) and angles (°) for chloro(2,2,2-trifluoroethyl isocyanide)gold (**6**)

Au-C(1)	1.95(2)
Au–Cl(1)	2.255(7)
C(1)–N(1)	1.09(3)
C(2)–N(1)	1.47(3)
C(1)–Au–Cl(1)	178.4(6)
N(1)–C(1)–Au	179(2)
C(1)–N(1)–C(2)	178(2)

2.3. Dinuclear complexes of 2,2,2-trifluoroethyl isocyanide

The most remarkable property of the trifluoromethyl isocyanide ligand is its great tendency to occupy the bridging position in dinuclear and trinuclear complexes giving raise to molecular structures not observed with other isocyanide ligands or the carbonyl ligand [1]. Especially interesting in this context are dinuclear complexes of molybdenum and tungsten as they are the only examples with a μ_2-η^2 coordination of the trifluoromethyl isocyanide ligand [36]. In addition a C–C coupling reaction of the trifluoromethyl isocyanide ligand forming a 1,4-dizabutatrien ligand was observed [37] (Scheme 3).

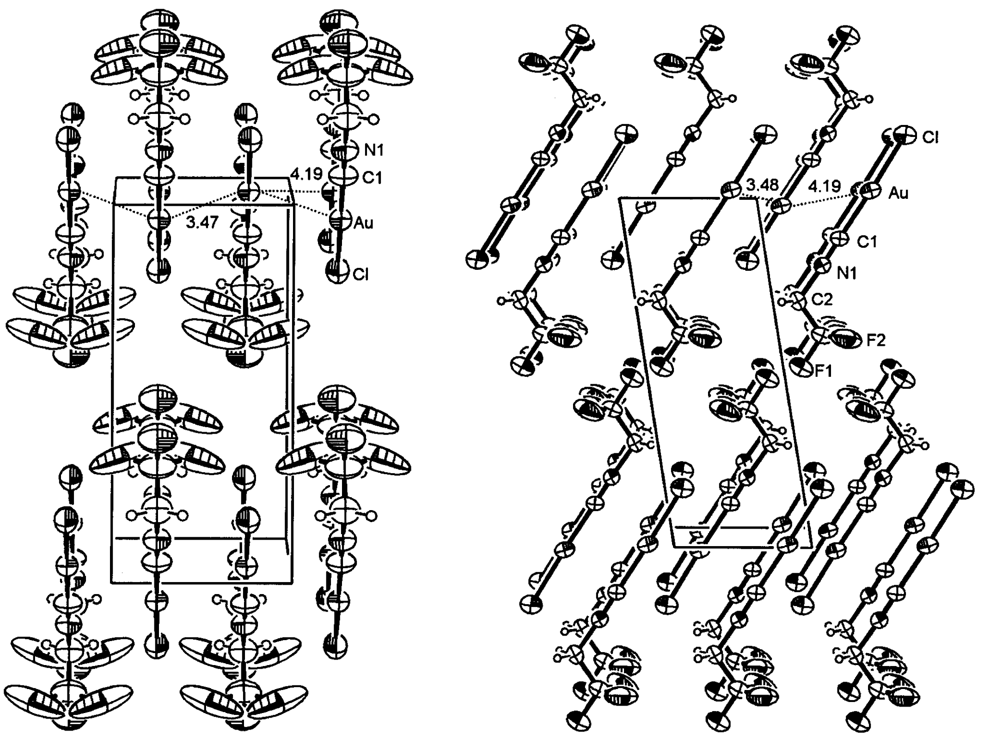


Fig. 2. Cell Plot (ORTEP [47]) of $ClAu(CN–CH_2–CF_3)$ (**6**); left normal to 100, right normal to 010.

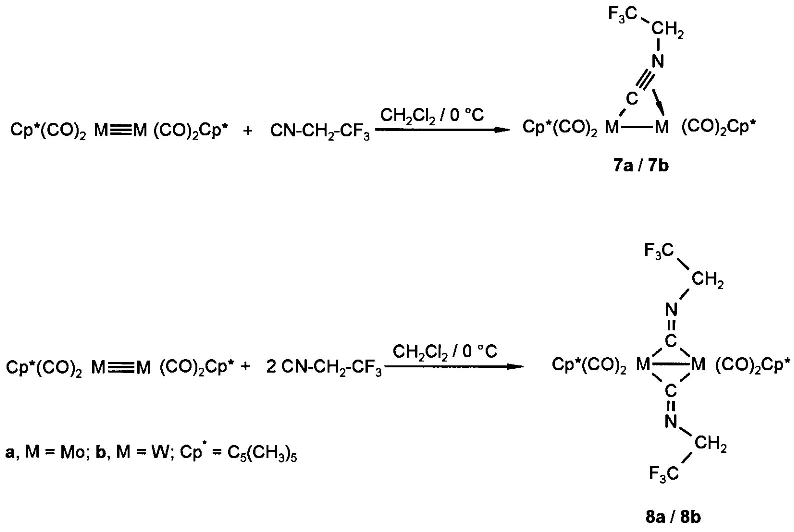
The reaction products of $[Cp^*M(CO)_2]_2$ (M = Mo, W) with 2,2,2-trifluoroethyl isocyanide strongly depend on the reaction conditions. If a 1:1 molar ratio is applied the only product isolated from the reaction mixture by crystallization at −20°C is $Cp^*_2M_2(CO)_2(\mu_2\text{-}\eta^2\text{-}CN\text{-}CH_2\text{–}CF_3)$ (**7**) (**a** M = Mo, **b** M = W). According to the spectroscopic data **7** contains two inequivalent $Cp^*M(CO)_2$ units. The ^1H- and $^{13}C\text{-}\{^1H\}$-NMR spectra exhibit two sets of signals of the chemically inequivalent pentamethylcyclopentadienyl ligands and four signals for the carbonyl carbon atoms. The remaining signals at 53.0 (qua, $^2J_{CF} = 32$ Hz), 123.7 (qua, $^1J_{CF} = 281$ Hz) and 240.6 (s) can be assigned to the carbon atoms of the isocyanide ligands of **7a**. Due to the C_1 symmetry of the molecule the two methylene carbon atoms are nonequivalent giving raise to a ABX_3 pattern. Consequently four CO stretching vibrations are observed in the IR spectrum in addition to a weak absorption at 1649 and 1582 cm^{-1} for **7a** and **b**, respectively, which can be assigned to the N=C stretching mode of the μ_2-η^2 coordinated isocyanide ligand. The spectroscopic data of **7** are in accordance with those observed for previously synthesized μ_2-η^2-isocyanide(tetracarbonyl)-bis(η^5 - cyclopentadienyl) - dimolybdenum complexes characterized by X-ray crystallography [38,39].

If an excess of the isocyanide is used bis[dicarbonyl(η^5 - pentamethylcyclopentadienyl)(μ_2 - η^2 - 2,2,2-trifluoroethyl isocyanide)molybdenum] (**8a**) and bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)(μ_2-η^2-2,2,2-trifluoroethyl isocyanide)tungsten] (**8b**) are obtained as red crystals. In accordance with the expected C_i symmetry of the molecule the NMR spectra exhibit only one set of signals for the Cp* and carbonyl ligands, respectively. The resonance of the bridging isocyanide carbon atom is observed at very low field at 278.7 and 269.8 ppm for **8a** and **b**. The IR spectra of **8a** and **b** exhibit the two expected CO stretching modes and one absorption for the C=N stretching. **8a** crystallizes orthorhombic, space group *Pcab* (no. 61) with half a molecule in the asymmetric unit. As the refinement of the CF_3 group was unstable it was refined as a rigid group using the geometrical parameters of $CF_3\text{–}CH_2\text{–}NC$ [19]. The molecular structure is depicted in Fig. 3. Selected bond lengths and angles are listed in Table 7. Like $[Cp^*Mo(CO)_2(\mu_2\text{-}CNCF_3)]_2$ [36] **8a** possesses crystallographic C_i symmetry.

The Mo–Mo distance in **8a** is almost the same as in $[Cp^*Mo(CO)_2(\mu_2\text{-}CNCF_3)]_2$ but much shorter than in $[CpMo(CO)_3]_2$ (3.255(1)) [40], $[Cp_2Mo_2(CO)_5(CNCH_3)]$ (3.230(1)) [41] and $[CpMo(CO)_2(CN\text{-}t\text{-}Bu)]_2$ (3.221(3)) [39] which possess only terminal ligands. The difference in Mo–C bond lengths to isocyanide ligands in **8a** is only 0.07 Å whereas the isocyanide bridges in $[Cp^*Mo(CO)_2(\mu_2\text{-}CNCF_3)]_2$ are strongly asymmetric with a difference in bond lengths of 0.23 Å. Consequently, the two Mo–C–N bond angles in **8a** are more alike than those in $[Cp^*Mo(CO)_2(\mu_2\text{-}CNCF_3)]_2$. In contrast to $[CpMo(CO)_2(\mu_2\text{-}CNCF_3)]_2$ **8a** shows no tendency of the isocyanide ligands to dimerize forming a diazabutatrien ligand [37].

3. Conclusions

2,2,2-Trifluoroethyl isocyanide and 1H,1H-perfluorooctyl isocyanide can easily be synthesized from commercially available starting materials. Although they are not as strong π accepting ligands as trifluoromethyl isocyanide they might have a brought use as ligands in organometallic chemistry as their



Scheme 3.

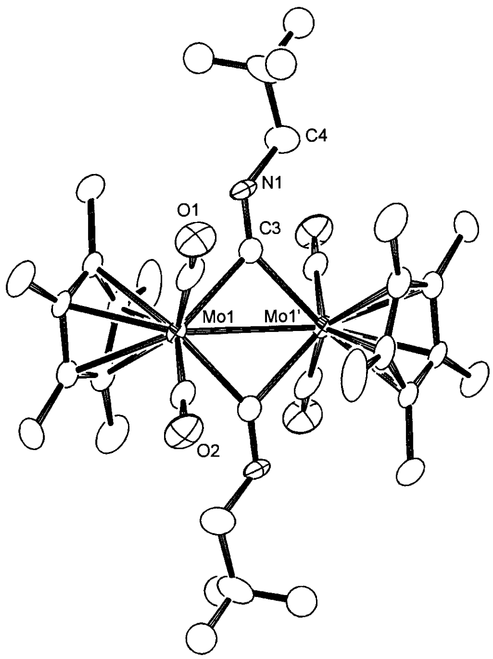


Fig. 3. Molecular structure (ORTEP [47]) [Cp*M(CO)$_2$-(CN–CH$_2$–CF$_3$)]$_2$ (**8a**).

Table 7
Selected bond lengths (Å) and angles (°) for [CpMo(CO)$_2$-(CN–CH$_2$CF$_3$)]$_2$ (**8a**) [a]

Mo(1)–C(1)	1.949(11)
Mo(1)–C(2)	1.971(9)
Mo(1)–C(3) # 1	2.167(9)
Mo(1)–C(3)	2.237(9)
Mo(1)–Mo(1) # 1	3.0961(13)
C(3)–N(1)	1.219(11)
N(1)–C(4)	1.418(11)
N(1)–C(3)–Mo(1) # 1	143.1(7)
N(1)–C(3)–Mo(1)	127.5(7)
Mo(1) # 1–C(3)–Mo(1)	89.3(3)
C(3)–N(1)–C(4)	125.9(8)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x+1$, $-y$, $-z$.

ligand behavior lies in between common alkyl isocyanides and perfluorinated isocyanides.

4. Experimental

2,2,2-Trifluoroethyl isocyanide was prepared from 2,2,2-trifluoroethyl amine via 2,2,2-trifluoroethyl formamide [14]. The metal carbonyl derivatives (CO)$_5$Cr(η^2-C$_8$H$_{14}$) [42], Cp*Mn(CO)$_3$ [43], (CO)$_3$W(η^6-C$_7$H$_8$) [44], (CO)$_3$Mo(η^6-C$_7$H$_8$) [44], [Cp*W(CO)$_2$]$_2$ [45] and [Cp*Mo(CO)$_2$]$_2$ [45] were prepared by cited published procedures. All reactions were carried out in dry solvents under argon by standard Schlenk and vacuum-line techniques.

The NMR spectra were recorded using a JEOL Lambda FX400 (400MHz) spectrometer. Infrared spectra were measured using a Perkin–Elmer 883 e.g. 983 instrument. Mass spectra were recorded with a Varian MAT 711 (70 eV) spectrometer.

4.1. *N-1,1-H-Perfluorooctylformamide (**1**)*

The preparation of **1** was analogous to 2,2,2-trifluoroethyl formamide [14].

N-1,1-H-Perfluorooctyl amine (4.6 g (11.53 mmol)) was dissolved in 10 ml diethylether. Formylacetate (2 g (22.7 mmol)) was added at 0°C. After the solution was stirred an additional hour the solvent and the acetic acid was removed under vacuum to yield 43.5 g (91.3%) as colorless crystals, m.p. 72°C. ^{1}H-NMR (CDCl$_3$): $\delta = 3.99$ (td, CH$_2$, $^3J_{H-F} = 8$, $^3J_{H-H} = 6$ Hz), 5.76 (1H, NH), 8.26 (1H, CHO). ^{19}F-NMR (CDCl$_3$): $\delta = -124.8$ (2F, CF$_2$), -121.9 (2F, CF$_2$), -121.4 (2F, CF$_2$), -120.7 (2F, CF$_2$), $-120{,}5$ (2F, CF$_2$), -116.8 (2F, CF$_2$), -79.5 (3F, CF$_3$).

4.2. *1,1-H-Perfluorooctyl isocyanide (**2**)*

The preparation occurred by a classical Ugi-synthesis with the formamide **1** and POCl$_3$ as dehydrating reagent. Compound **1** (1 g (2.34 mmol)) and triethyl amine (1.18 g (11.7 mmol) was suspended in CH$_2$Cl$_2$. After the suspension was cooled to -25°C POCl$_3$ (0.43 g (3 mmol) was added during a period of 1 h. The solution was allowed to warm to ambient temperature. The reaction mixture was washed with a saturated sodium carbonate solution (20 ml) and twice with water (20 ml). The organic layer was dried over sodium sulfate. Fractional condensation under vacuum (-196/-30°C) yielded **2**, 570 mg (59.5%), as colorless crystals in the trap kept at -30°C, m.p. 38°C. ^{1}H-NMR (CDCl$_3$): $\delta = 4.08$ (2H, t, $^3J_{HF} = 13.1$ Hz, CH$_2$). ^{19}F-NMR (CDCl$_3$): $\delta = -125.0$ (2F, δ-CF$_2$), -121.6 (2F, γ-CF$_2$), -121.5 (2F, ζ-CF$_2$), -120.8 (2F, ε-CF$_2$), -120.6 (2F, β-CF$_2$), -115.8 (2F, α-CF$_2$), -79.6 (3F, CF$_3$). ^{13}C-NMR (CDCl$_3$): $\delta = 42.3$ (t, $^2J_{CF} = 25.9$ Hz, CH$_2$), 108.0, 110.4, 113.2, 115.4, 118.4,119.1 (m, 6 CF$_2$ u. CF$_3$), 165.8 (CN). ^{13}C-{^{19}F}-NMR (CDCl$_3$): $\delta = 42.5$ (t, $^1J_{CH} = 146.6$ Hz, CH$_2$), 108.5 (δ-CF$_2$), 110.3 (γ-CF$_2$), 110.8 (ε-CF$_2$), 110.8 (ζ-CF$_2$), (β-CF$_2$), 113.2 (t, $^2J_{CH} = 4.4$ Hz, α-CF$_2$), 117.3 (s, CF$_3$), 165.7 (CN). MS (70 eV): $m/z = 409$ (1%, M^+), 390 (14%, M$^+$ − HF), 190 (9%, C$_3$F$_7^+$), 119 (25%, C$_2$F$_5^+$), 90 (100%, CNCH$_2$CF$_2^+$), 69 (51%, CF$_3^+$). IR (KBr): $\nu = 2169$ m (CN), 1236 m (CF), 1206 s (CF), 1147 s (CF). IR (CH$_2$Cl$_2$): $\nu = 2157$ s (CN). Anal. Calc. for C$_9$F$_{15}$H$_2$N (409.1 g mol^{-1}): C, 26.42; H, 0.49, N, 3.42. Found: C, 26.39; H, 1.21; N, 3.51%.

4.3. *Pentacarbonyl(2,2,2-trifluoroethyl isocyanide)chromium (**3a**)*

$(CO)_5Cr(\eta^2\text{-}C_8H_{14})$ (152 mg (0.5 mmol)) was dissolved in CH_2Cl_2. 2,2,2-Trifluoroethyl isocyanide (65.4 mg (0.6 mmol)) was added and the solution was stirred until the color turned from yellow to colorless. All solvent and some $Cr(CO)_6$ was removed under vacuum to yield 102 mg (68%) colorless crystals, m.p. 42°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.16$ (2H, q, $^3J_{FH} = 7.6$ Hz; CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -70.9$ (3F, t, $^3J_{FH} = 7.6$ Hz; CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta = 46.3$ (q, $^2J_{CF} = 39.3$ Hz; CH_2), 121.2 (q, $^1J_{CF} = 281.6$ Hz; CF_3), 175.3 (CN), 213.9 (CO_{cis}), 215.5 (CO_{trans}). MS (70 eV): $m/z =$ 301 (16%, M^+), 189 (21%, $M^+ - 4CO$), 161 (100%, $CrCNCH_2CF_3^+$); 64 (12%, $CH_2CF_2^+$), 52 (38%, Cr^+). IR (CH_2Cl_2): $\nu = 2164$ s (CN), 2066 s (CO), 1954 vs (CO). Anal. Calc. for $C_8CrF_3H_2NO_5$ (301.1 g mol^{-1}): C, 31.91; H, 0.67; N, 4.65. Found: C, 31.35; H, 1.16; N, 4.61%.

4.4. *Pentacarbonyl(1,1-H-perfluoroctyl isocyanide)chromium (**3b**)*

$Cr(CO)_6$ (135 mg (0.61 mmol)) was dissolved in 60 ml of THF and irradiated for 6 h using a high pressure Hg lamp. The carbon monoxide formed was removed occasionally under vacuum. 1,1-H-perfluorooctyl isocyanide (251 mg (0.61 mmol)) was added. The reaction mixture was stirred until the orange color of the THF complex had disappeared completely. The solvent and $Cr(CO)_6$ was removed in vacuum to yield 248 mg (67.2%) colorless crystals, m.p. 71°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.30$ (2H, t, $^3J_{FH} = 11.9$ Hz, CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -124.9$ (2F, CF_2), -121.5 (2F, CF_2), -121.4 (2F, CF_2), -120.7 (2F, CF_2), $-120{,}6$ (2F, CF_2), -115.5 (2F, CF_2), -79.5 (3F, CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta = 44.9$ (t, $^2J_{CF} = 28.6$ Hz, CH_2), 103.5, 108.0, 110.5, 113.3, 115.7 (m, 6 CF_2/CF_3), 176.4 (CN), 213.9 (CO_{cis}), 215.4 (CO_{trans}). MS (70 eV): $m/z = 601$ (10%, M^+), 489 (10%, $M^+ - 4CO$), 461 (100%, $M^+ - 5CO$), 52 (39%, Cr^+). IR (CH_2Cl_2): $\nu = 2165$ m (CN), 2064 m (CO), 1956 vs (CO). IR (KBr): $\nu = 2166$ s (CN), 2076 vs (CO), 1983 s (CO), 1946 vs (CO),1920 vs (CO), 1241 s, 1210 vs, 1150 vs. Anal. Calc. for $C_{14}CrF_{15}H_2NO_5$ (601.2 g mol^{-1}): C, 27.97; H, 0.34; N, 2.33. Found: C, 27.27; H, 1.66; N, 5.14%.

4.5. *fac-(Tricarbonyl)tris(2,2,2-trifluoroethyl isocyanide)tungsten (**4b**)*

$(CO)_3W(\eta^6\text{-}C_7H_8)$ (240 mg (0.67 mmol)) was dissolved in CH_2Cl_2 (10 ml). 2,2,2-Trifluoroethyl isocyanide (280 mg (2.57 mmol)) was added and the solution was stirred for 1 h. Most of the dichloromethane was removed in vacuum, *n*-pentane was added and the solution was stored at -30°C to crystallize *fac*-(tricarbonyl)tris(2,2,2-trifluoroethyl isocyanide)tungsten (**4b**). Purification by sublimation (80°C, 10^{-3} mbar) yielded 296 mg (74.3%) as pale yellow crystals, m.p. 102°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.18$ (2H, q, $^3J_{FH} = 7.6$ Hz; CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -71.2$ (3F, t, $^3J_{FH} = 7.6$ Hz; CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta = 45.7$ (q, $^2J_{CF} =$ 39.0 Hz;CH_2), 121.6 (q, $^1J_{CF} = 280.0$ Hz, CF_3), 162.1 (t, $^1J_{C^{183}W} = 114.5$Hz; CN), 200.2 (t, $^1J_{C^{183}W} = 133.1$ Hz; CO). MS (70 eV): $m/z = 595$ (46%, M^+), 567 (21%, $M^+ - CO$), 539 (92%, $M^+ - 2CO$), 511 (2%, $M^+ -$ 3CO), 447 (100%, $M^+ - 3CO - CH_2CF_2$), 90 (13%, $CNCH_2CF_2^+$), 64 (43%, $CH_2CF_2^+$). IR (*n*-pentane): $\nu =$ 2165 m (CN), 2106 w (CN), 1952 vs (CO), 1902 vs (CO). IR (KBr): $\nu = 2176$ s (CN), 2128 s (CN), 1928 vs (CO), 1865 vs (CO). Anal. Calc. for $C_{12}F_9H_6N_3O_3W$ (595.03 g mol^{-1}): C, 24.22; H, 1.02; N, 7.06. Found: C, 24.23; H, 1.94; N, 7.04%.

4.6. *fac-(Tricarbonyl)tris(2,2,2-trifluoroethyl isocyanide)molybdenum (**4a**)*

Compound **4a** was prepared analogous to **4b**. Crystallization from pentane yielded 227 mg (51.9%) pale yellow crystals, m.p. 86°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.19$ (2H, q, $^3J_{FH} = 7.7$ Hz; CH_2). ^{19}F-NMR ($CDCl_3$): $\delta =$ -71.3 (3F, t, $^3J_{FH} = 7.7$ Hz; CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta = 46.7$ (q, $^2J_{CF} = 38.4$ Hz; CH_2), 122.6 (q, $^1J_{CF} = 278.0$ Hz;CF_3), 173.3 (CN), 210.9 (CO). MS (70 eV): $m/z = 509$ (18%, M^+), 453 (25%, $M^+ - 2CO$), 425 (32%, $M^+ - 3CO$), 316 (90%, $Mo(CNCH_2CF_3)_2^+$), 207 (100%, $MoCNCH_2CF_3^+$), 98 (10%, Mo^+), 64 (4%, $CH_2CF_2^+$). IR (CH_2Cl_2): $\nu = 2164$ m (CN), 2112 s (CN), 1953 vs (CO), 1899 s (CO). IR (KBr): $\nu = 2173$ s (CN), 2112 s (CN), 1936 vs (CO), 1936 vs (CO), 1865 vs (CO). Anal. Calc. for $C_{12}F_9H_6MoN_3O_3$ (507.12 g mol^{-1}): C, 28.42; H, 1.19; N, 8.29. Found: C, 28.21; H, 2.03; N, 8.18%.

4.7. *fac-(Tricarbonyl)tris(1,1-H-perfluorooctyl isocyanide)tungsten (**4c**)*

Compound **4c** was prepared analogous to **4b**. Recrystallization from CH_2Cl_2 gave 143 mg (73.6%), m.p. (dec.) 102°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.21$ (2H, q, $^3J_{HF} = 12.8$ Hz, CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -125.1$ (2F, CF_2), -121.7 (2F, CF_2), -121.5 (2F, CF_2), -121.0 (2F, CF_2), -120.8 (2F, CF_2), -116.0 (2 F, CF_2), -79.6 (3F,CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta =$ 46.1 (t, $^2J_{CF} = 27.0$ Hz, CH_2), 110.0, 112.7, 115.4, 116.9 (m, 6 CF_2 u. CF_3), 175.7 (CN), 202.4 (CO). MS (70 eV): $m/z = 1495$ (41%, M^+), 1467 (100%, $M^+ - CO$), 1439 (16%, $M^+ - 2CO$), 1411 (10%, $M^+ - 3CO$), 982 (44%, $W(CNCH_2C_7F_{15})_2^+ - HF$), 314 (22%, $(CF_2)_6CH_2^+$), 169 (3%, $CF_3CF_2CF_2^+$). IR (KBr): $\nu = 2186$ m (CN), 2127 s (CN), 1982 s (CO), 1874 vs (CO), 1238 s, 1207 vs, 1148 vs. Anal. Calc. for $C_{30}F_{45}H_6N_3O_3W$ (1495.2 g mol^{-1}): C, 24.09; H, 0.40; N, 2.81. Found: C, 23.94; H, 2.64; N, 4.73%.

*4.8. Dicarbonyl(2,2,2-trifluorethyl isocyanide)-(η^5-pentamethylcyclopentadienyl)manganese (**5**)*

Tricarbonyl(η^5 - pentamethylcyclopentadienyl)manganese (340 mg (1.25 mmol)) was dissolved in dry THF. After irradiation by UV light for about 4 h 2,2,2-trifluoroethyl isocyanide (170 mg (1.56 mmol)) was added. The solution was stirred at ambient temperature for 1 h. The solvent was removed under vacuum. The residue was dissolved in *n*-pentane and purified by chromatography (Silica, *n*-pentane). Crystallization at −30°C gave 212 mg (47.2%) yellow crystals, m.p. 56 − 57°C. ^{1}H-NMR ($CDCl_3$): $\delta = 1.78$ (15H, s, CH_3), 4.07 (2H, q, $^3J_{HF} = 8.0$, CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -71.7$ (3F, t, $^3J_{HF} = 8.0$ Hz, CF_3). ^{13}C-{^{1}H}-NMR ($CDCl_3$): $\delta = 10.4$ (s, CH_3), 46.9 (q, $^2J_{CF} = 37.1$ Hz; CH_2), 95.0 (s, Cp), 122.5 (q, $^1J_{CF} = 278.0$; CF_3), 207.0 (CN), 229.9 (CO). MS (70 eV): $m/z = 355$ (26%, M^+), 299 (100%, $M^+ - 2CO$), 190 (71%, Cp^*Mn^+),135 (86%, Cp^{*+}). IR (pentane): $\tilde{\nu} = 2104$ m (CN), 1998 vs (CO), 1924 s (CO). Anal. Calc. for $C_{15}F_3H_{17}$ $MnNO_2$ (355.24 g mol^{-1}): C, 50.71; H, 4.82; N, 3.94. Found: C, 50.37; H, 5.11; N, 3.81%.

*4.9. Chloro(2,2,2-trifluoroethyl isocyanide)gold (**6**)*

Chloro(dimethylsulfide)gold (92 mg (0.312 mmol)) was dissolved in dry CH_2Cl_2. 2,2,2-Trifluoroethyl isocyanide (60 mg (5.50 mmol)) was added and the solution was stirred at ambient temperature for 4 h. The solution was reduced under vacuum. Crystallization at −30°C gave 28 mg (26.3%) as colorless crystals. ^{19}F-NMR ($CDCl_3$): $\delta = -71.0$ (3F, t, $^3J_{HF} = 8$ Hz, CF_3).

Table 4
Crystal data and structure refinement for *fac*-$(CO)_3W(CN–CH_2–CF_3)_3$ (**4a**), $ClAu(CN–CH_2–CF_3)$ (**6**) and $[CpMo(CO)_2(CN–CH_2CF_3)]_2$ (**8a**)

	4a	**6**	**8a**
Empirical formula	$C_{12}H_6F_9MoN_3O_3$	$C_3H_2AuClF_3N$	$C_{30}H_{34}F_6Mo_2N_2O_4$
Formula weight	507.14	341.47	792.47
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/m$	$P2_1/m$	*Pcab*
Unit cell dimensions			
a (Å)	5.7110(13)	4.774(2)	9.316(2)
b (Å)	15.357(3)	5.824(2)	18.400(3)
c (Å)	10.554(2)	12.308(2)	18.637(3)
α (°)	90	90	90
β (°)	103.42(2)	99.32(2)	90
γ (°)	90	90	90
Volume (Å^3)	900.4(3)	337.69(19)	3194.7(10)
Z	2	2	4
D_{calc} (Mg m^{-3})	1.871	3.358	1.648
Absorption coefficient (mm^{-1})	0.836	22.143	0.857
F(000)	492	300	1592
Crystal size (mm^3)	$0.4 \times 0.2 \times 0.1$	$0.7 \times 0.3 \times 0.1$	$0.25 \times 0.20 \times 0.20$
θ range for data collection (°)	2.39–25.00	3.35–29.97	2.19–24.99
Index ranges	$-6 \le h \le 0$, $-18 \le k \le 18$, $-12 \le l \le 12$	$-6 \le h \le 0$, $-8 \le k \le 8$, $-17 \le l \le 17$	$0 \le h \le 11$, $0 \le k \le 21$, $-20 \le l \le 22$
Reflections collected	3569	2175	4965
Independent reflections	1653 [$R_{int} = 0.0524$]	1074 [$R_{int} = 0.0589$]	2812 [$R_{int} = 0.0476$]
Completeness to $\theta = 25.00°$ (%)	99.9	99.9	100.0
Absorption correction	No	PSI scan	No
Max. and min. transmission		0.98169 and 0.45598	
Refinement method	Full-matrix least-squares on F^2, SHELXL-97	Full-matrix least-squares on F^2, SHELXL-97	Full-matrix least-squares on F^2, SHELXL-97
Data/restraints/parameters	1653/0/139	1074/0/53	2812/0/190
Goodness-of-fit on F_2	1.041	1.060	1.106
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0595$, $wR_2 = 0.1488$	$R_1 = 0.0643$, $wR_2 = 0.1647$	$R_1 = 0.0561$, $wR_2 = 0.1422$
R indices (all data)	$R_1 = 0.0943$, $wR_2 = 0.1744$	$R_1 = 0.0948$, $wR_2 = 0.1808$	$R_1 = 0.1506$, $wR_2 = 0.1676$
Extinction coefficient		0.012(4)	
Largest difference peak and hole (e Å^{-3})	0.938 and −0.536	3.215 and −2.446	1.806 and −0.810

*4.10. Tetracarbonyl(μ_2-η^2-2,2,2-trifluoroethyl isocyanide)bis(η^5-pentamethylcyclopentadienyl)-dimolybdenum (**7a**)*

Bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)-molybdenum] (232 mg (0.404 mmol)) was dissolved in CH_2Cl_2. The solution was cooled to 0°C and 2,2,2-trifluoroethyl isocyanide (44 mg, 0.404 mmol) was added. After the solution was stirred for 30 min *n*-heptane (10 ml) was added. CH_2Cl_2 was removed in vacuum. Crystallization from *n*-heptane gave 140 mg (50.7%) brown crystals, m.p. (dec.) 125. ^{1}H-NMR (CD_2Cl_2): $\delta = 1.81$ (15H, s, CH_3), 1.93 (15H, s, CH_3), 3.76 (1H, $^2J_{HH} = 13.7$ Hz, $^3J_{HF} = 9.0$ Hz, CH_2), 4.23 (1H, $^2J_{HH} = 13.7$ Hz, $^3J_{HF} = 9.0$ Hz, CH_2). ^{19}F-NMR (CD_2Cl_2): $\delta = -68.7$ (3F, t, $^3J_{FH} = 9.0$ Hz; CF_3). ^{13}C-{^{1}H}-NMR (CD_2Cl_2):$\delta = 10.5$ (s, C_5Me_5), 11.2 (s, C_5Me_5), 53.0 (q, $^2J_{CF} = 31.5$ Hz, CH_2), 105.1 (s, CH_3), 106.8 (s, CH_3), 123.7 (q, $^1J_{CF} = 280.9$ Hz), 234.4 (s, CO), 234.9 (s, CO), 240.6 (s, CN), 248.1 (s, CO), 249.3 (s, CO). MS (70 eV): $m/z = 683$ (M^+), 655 ($M^+ - CO$), 571 ($M^+ - 4CO$), 109 ($CNCH_2CF_3^+$), 69 (CF_3^+). IR (CH_2Cl_2): $\nu = 1953$ s (CO), 1896 vs (CO), 1871 s (CO), 1816 s (CO), 1649 w (CN). IR (KBr): $\nu = 1959$ vs (CO), 1898 vs (CO), 1863 vs (CO), 1822 vs (CO), 1647 m (CN). Anal. Calc. for $C_{27}F_3H_{32}Mo_2NO_4$ (683.4 g mol^{-1}): C, 47.45; H, 4.72; N, 2.06. Found: C, 46.52; H, 4.74; N, 2.64%.

*4.11. Tetracarbonyl(μ_2-η^2-2,2,2-trifluoroethyl isocyanide)bis(η^5-pentamethylcyclopentadienyl)-ditungsten (**7b**)*

Compound **7b** was prepared analogous to **7a**. Crystallization from *n*-heptane gave 220 mg (34.5%) brown crystals, m.p. (dec.) 141°C . ^{1}H-NMR ($CDCl_3$): $\delta = 3.64$ (1H, $^2J_{HH} = 14.2$ Hz, $^3J_{HF} = 9.0$ Hz, CH_2), 4.09 (1H, $^2J_{HH} = 14.2$ Hz, $^3J_{HF} = 9.0$ Hz, CH_2). ^{19}F-NMR ($CDCl_3$): $\delta = -68.6$ (3F, t, $^3J_{HF} = 10.0$ Hz, CF_3). MS (70 eV): $m/z = 859$ (M^+), 803 ($M^+ - 2CO$), 747 ($M^+ - 4CO$), 683 (100%, $M^+ - 2CO/C_5(CH_3)_5$), 135 ($C_5(CH_3)_5^+$). IR (CH_2Cl_2): $\nu = 1948$ s (CO), 1924 s (CO), 1888 vs (CO), 1861 w (CO), 1804 s (CO), 1582 w (CN). IR (KBr): $\nu = 1955$ s (CO), 1926 m (CO), 1890 vs (CO), 1872 w (CO), 1809 s (CO), 1593 m (CN). Anal. Calc. for $C_{27}F_3H_{32}NO_4W_2$ (859.25 g mol^{-1}): C, 37.74; H, 3.75; N, 1.63. Found: C, 35.45; H, 4.07; N, 1.53%.

*4.12. Bis[dicarbonyl(μ_2-2,2,2-trifluoroethyl isocyanide)-(η^5-pentamethylcyclopentadienyl)-tungsten] (**8b**)*

Bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)tungsten] (328 mg (0.44 mmol)) was dissolved in CH_2Cl_2. The solution was cooled to 0°C and 2,2,2-trifluoroethyl isocyanide (143 mg (1.3 mmol)) was added. After the solution was stirred for 1 h *n*-pentane was added. The flask was stored at −30°C to yield 222 mg (52.3%) as orange crystals, m.p. (dec.) 162°C. ^{1}H-NMR ($CDCl_3$): $\delta = 1.84$ (15H, s, CH_3), 3.16 (2H, q, $^3J_{FH} = 9.2$ Hz, CH_2). ^{19}F-NMR ($CDCl_3$):$\delta = -69.4$ (3F, t, $^3J_{FH} = 9.2$ Hz; CF_3), ^{13}C-{^{1}H}-NMR (CD_2Cl_2): $\delta = 10.5$ (s, CH_3), 64.3 (q, $^2J_{CF} = 30.4$ Hz; CH_2), 106.3 (s, Cp), 125.7 (q, $^1J_{CF} = 278.6$; CF_3), 228.3 (CO), 269.8 (CN). MS (70 eV): $m/z = 968$ (4%, M^+), 940 (34%, $M^+ - CO$), 884 (100%, $M^+ - 3CO$), 803 (76%, $M^+ - 2CO/CNCH_2CF_3$), 747 (46%, $M^+ - 4$ $CO/CNCH_2CF_3$), 135 (6%, $C_5(CH_3)_5^+$), 64 (6%, $CH_2CF_2^+$). IR (KBr): $\nu = 1915$ vs (CO), 1863 vs (CO), 1630 s (CN). Anal. Calc. for $C_{30}F_6H_{34}N_2O_4W_2$ (968.3 g mol^{-1}): C, 37.21; H, 3.53; N, 2.89. Found: C, 36.42; H, 3.85; N, 3.15%.

*4.13. Bis[dicarbonyl(μ_2-2,2,2-trifluoroethyl isocyanide)-(η^5-pentamethylcyclopentadienyl)-molybdenum] (**8a**)*

Compound **8a** was prepared analogous to **8b**. Crystallization from *n*-pentane yielded 343 mg (61.0%) red crystals, m.p. (dec.) 146°C. ^{1}H-NMR (CD_2Cl_2): $\delta = 1.76$ (30H, s, CH_3), 4.65 (4H, q, $^3J_{FH} = 9.5$ Hz, CH_2). ^{19}F-NMR (CD_2Cl_2): $\delta = -69.2$ (3F, t, $^3J_{FH} = 9.5$ Hz; CF_3). ^{13}C-{^{1}H}-NMR (CD_2Cl_2): $\delta = 10.3$ (s, CH_3), 61.6 (q, $^2J_{CF} = 33.5$ Hz; CH_2), 106.7 (s, Cp), 123.3 (3 F, q, $^1J_{CF} = 276.3$ Hz,CF_3), 237.4 (CO), 278.7 (CN). MS (70 eV): $m/z = 792$ (M^+), 764 ($M^+ - CO$), 708 ($M^+ - 3CO$), 680 ($M^+ - 4CO$), 109 ($CNCH_2CF_3^+$), 69 (CF_3^+). IR (CH_2Cl_2): $\nu = 1927$ vs (CO), 1875 s (CO), 1641 m (CN). IR (KBr): $\nu = 1922$ vs (CO), 1867 vs (CO), 1648 m (CN). Anal. Calc. for $C_{30}F_6H_{34}$ $Mo_2N_2O_4$ (792.5 g mol^{-1}): C, 45.35; H, 4.32; N, 3.53. Found: C, 42.80; H, 4.36; N, 3.54%.

4.14. X-ray crystallographic study

Suitable crystals of **4b**, **6** and **8a** were obtained by crystallization from *n*-pentane–dichloromethane at −20°C. Details on the data collection, structure solution and refinement are summarized in Table 4. Data collection: STOE 4-circle diffractometer, Mo–K_α, ω scan. Structure solution by direct methods (SHELXS-97 [46]), structure refinement, full-matrix least-squares on F_o^2 (SHELXL-97 [46]) using anisotropic thermal parameters for non hydrogen atoms, hydrogen atom on calculated position with r(C–H) = 98 pm and U(H) = $1.2U_{eq}$(C). ORTEP [47] was used for molecular drawings.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 143385–143387. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie and the Deutschen Forschungsgemeinschaft (DFG).

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