Synthesis and Characterization of a New Family of Square-Planar Nickel(II) Carbonyl Derivatives

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Abstract: The reaction of $[NBu_4]_2[Ni(C_6F_5)_4]$ (**1**) with solutions of dry HCl(g) in Et_2O results in the protonolysis of two $Ni-C_6F_5$ bonds giving $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (**2a**) together with the stoichiometrically required amount of C_6F_5H. Compound **2a** reacts with $AgClO_4$ in THF to give *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (**3**). Reacting **3** with phosphonium halides, $[PPh_3Me]X$, gives dinuclear compounds $[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]$ (X = Br (**2b**) or I (**2c**)). Solutions of compounds **2** in CH_2Cl_2 at 0 °C do not react with excess CN*t*Bu, but do react with CO (1 atm) to split the bridges and form a series of terminal Ni^{II} carbonyl derivatives with general formula Q*cis*-$[Ni(C_6F_5)_2X(CO)]$ (**4**). The $\nu(CO)$ stretching frequencies of **4** in CH_2Cl_2 solution decrease in the order Cl ($2090\,cm^{-1}$) > Br ($2084\,cm^{-1}$) > I ($2073\,cm^{-1}$). Compounds **4** revert to the parent dinuclear species **2** on increasing the temperature or under reduced CO pressure. $[NBu_4]$*cis*-$[Ni(C_6F_5)_2Cl(CO)]$ (**4a**) reacts with AgC_6F_5 to give $[NBu_4][Ni(C_6F_5)_3(CO)]$ (**5**, $\nu_{CO}(CH_2Cl_2) = 2070\,cm^{-1}$). Compound **5** is also quantitatively formed (^{19}F NMR spectroscopy) by 1:1 reaction of **1** with $HCl(Et_2O)$ in CO atmosphere. Complex **3** reacts with CO at −78 °C to give *cis*-$[Ni(C_6F_5)_2(CO)_2]$ (**6**, $\nu_{CO}(CH_2Cl_2) = 2156, 2130\,cm^{-1}$), which easily decomposes by reductive elimination of $C_6F_5-C_6F_5$. Compounds **3** and **6** both react with CN*t*Bu to give *trans*-$[Ni(C_6F_5)_2(CNtBu)_2]$ (**7**). The solid-state structures of compounds **3**, **4b**, **6**, and **7** have been established by X-ray diffraction methods. Complexes **4**–**6** are rare examples of square-planar Ni^{II} carbonyl derivatives.

Keywords: carbonyl ligands · nickel · pentafluorophenyl ligands · structure elucidation

Introduction

The study of group trends are among the most useful tools at the chemist's disposal when trying to rationalize the chemical properties of the elements within the periodic table. Sometimes, however, the differences in the properties and chemical behavior of the elements for a given group outweigh their analogies. One clear example is found in the carbonyl chemistry of Group 10 elements. Thus, $[Ni(CO)_4]$ is a well-known, stable molecule prepared in 1890 by L. Mond and co-workers under very mild conditions.[1] In contrast, the heavier zerovalent homologues $[M(CO)_4]$ (M = Pd, Pt) are very unstable and can only be detected using low-temperature matrix techniques.[2] When moving to the oxidation state II, however, the reverse behavior is observed: the reasonably stable compounds $[\{PtCl_2(CO)\}_2(\mu\text{-}Cl)_2]$ and *cis*-$[PtCl_2(CO)_2]$ were prepared by P. Schützenberger as early as 1868,[3] while the related species $[NiCl_2(CO)]$ and $[NiCl_2(CO)_2]$ are detectable only at very low temperatures.[4] These are just a few of the many differences between the light and heavier elements of Groups 8–10 that have induced, and even justified, the empirical division traditionally adopted in iron group and platinum group metals.[5]

Some years ago, we reported the synthesis and characterization of the series of square-planar dicarbonyl complexes *cis*-$[M(C_6X_5)_2(CO)_2]$ (M = Pd, Pt; X = F, Cl).[6] Perhaps the most surprising aspect of this work was the high $\nu(CO)$ frequencies observed; these suggested the existence of "negligible metal-to-CO π back-bonding". In the years following this report, the chemistry of various metal carbonyl

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Table 1. IR data [cm^{-1}] for compounds **1**–**7** (KBr).

Compound	$\nu(C{\equiv}E)$[a]	ν(C–F)	X-sensitive[b]	other
$[NBu_4]_2[Ni(C_6F_5)_4]$ (**1**)	–	947	759	1485, 1443, 1051, 1035, 882 (NBu_4^+)
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (**2a**)	–	950	790 (sh), 779	1493, 1454, 1050, 881 (NBu_4^+), 323, 308 (Ni–Cl)
$[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Br)_2]$ (**2b**)	–	953	787, 782	1495, 1453, 1439, 1117, 1052, 897, 744, 720, 689, 509
$[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}I)_2]$ (**2c**)	–	951	785, 780	1495, 1452, 1439, 1116, 1052, 897, 744, 719, 689, 500
cis-$[Ni(C_6F_5)_2(thf)_2]$ (**3**)[c]	–	953	796 (sh), 786	1501, 1459, 1355, 1059, 1035, 877 (COC)
$[NBu_4]$*cis*-$[Ni(C_6F_5)_2Cl(CO)]$ (**4a**)	2096	953	790 (sh), 780	1500, 1456, 1054, 883 (NBu_4^+)
$[PPh_3Me]$*cis*-$[Ni(C_6F_5)_2Br(CO)]$ (**4b**)	2081	955	786 (sh), 780	1499, 1456, 1116, 1053, 901, 748, 720, 688, 503, 491
$[PPh_3Me]$*cis*-$[Ni(C_6F_5)_2I(CO)]$ (**4c**)	2069	954	784 (sh), 780	1497, 1457, 1116, 1052, 902, 747, 720, 688, 503, 492
$[NBu_4][Ni(C_6F_5)_3(CO)]$ (**5**)	2065	953	782 (sh), 778	1500, 1456, 1057, 1043, 884 (NBu_4^+), 528
cis-$[Ni(C_6F_5)_2(CO)_2]$ (**6**)	2162, 2138	957	796 (sh), 788	1505, 1464, 1079, 1062
trans-$[Ni(C_6F_5)_2(CN\mathit{t}Bu)_2]$ (**7**)	2209	957	776	1499, 1452, 1375, 1342, 1236, 1199, 1059, 1043, 541, 473, 456

[a] E = O or N. [b] Ref. [9]. [c] See also ref. [20].

Table 2. ^{19}F NMR data in solution (δ values in ppm referred to $CFCl_3$).

Compound	*o*-F	*m*-F	*p*-F
$[NBu_4]_2[Ni(C_6F_5)_4]$ (**1**)[a]	–114.3	–169.3	–168.7
$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (**2a**)[a]	–116.6	–167.5	–165.2
$[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Br)_2]$ (**2b**)[a]	–116.2	–166.7	–164.7
$[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}I)_2]$ (**2c**)[b]	–113.4	–165.3	–164.0
cis-$[Ni(C_6F_5)_2(thf)_2]$ (**3**)[a]	–118.8	–164.6	–160.5
$[NBu_4]$*cis*-$[Ni(C_6F_5)_2Cl(CO)]$ (**4a**)[a]	–118.0, –118.8	–164.7, –165.4	–161.5, –163.8
$[PPh_3Me]$*cis*-$[Ni(C_6F_5)_2Br(CO)]$ (**4b**)[a]	–117.9, –118.2	–164.7, –165.5	–161.6, –164.0
$[PPh_3Me]$*cis*-$[Ni(C_6F_5)_2I(CO)]$ (**4c**)[a]	–116.7, –118.6	–164.6, –165.6	–161.7, –164.1
$[NBu_4][Ni(C_6F_5)_3(CO)]$ (**5**)[a]	–118.3[c]	–165.1, –166.2	–162.6, –164.8
cis-$[Ni(C_6F_5)_2(CO)_2]$ (**6**)[b][d]	–118.9	–162.1	–157.2
trans-$[Ni(C_6F_5)_2(CN\mathit{t}Bu)_2]$ (**7**)[a]	–118.1,[e] –119.1[f]	–164.2,[e] –164.8[f]	–160.4,[e] –161.8[f]

[a] In [^{2}H]chloroform. [b] In [^{2}H]dichloromethane. [c] Complex signal centered at the given value. [d] Registered at –70 °C. [e] Majority species. [f] Minority species.

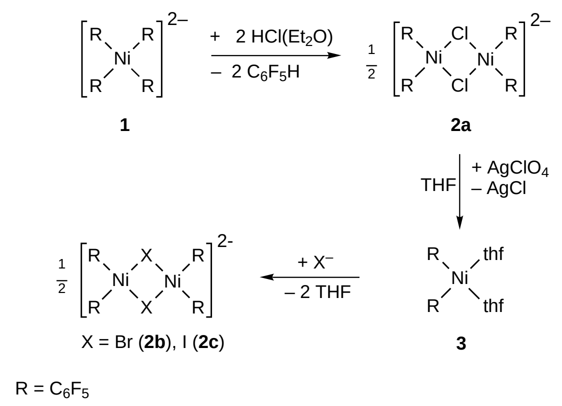
species in which the CO molecule behaves mainly as a σ-donor ligand (sometimes termed as "nonclassic" carbonyls) has been considerably and admirably expanded.[7] However, to the best of our knowledge, a parallel expansion of nickel(II) carbonyl chemistry has not occurred. We now report the synthesis and characterization of new square-planar carbonyl derivatives of nickel(II), which allow a comparison of the properties for all three Group 10 metals.

Abstract in Spanish: *Por reacción de* $[NBu_4]_2[Ni(C_6F_5)_4]$ (**1**) *con HCl(g) seco disuelto en* Et_2O*, se obtiene* $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (**2a**)*, junto con la cantidad requerida de* C_6F_5H*, como resultado de la protonolisis de dos enlaces* $Ni{-}C_6F_5$*. Por reacción de* **2a** *con* $AgClO_4$ *en THF, se obtiene cis-*$[Ni(C_6F_5)_2(thf)_2]$ (**3**)*. El tratamiento de* **3** *con sales de fosfonio,* $[PPh_3Me]X$*, da lugar a los compuestos dinucleares* $[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]$ *[X = Br* (**2b**)*, I* (**2c**)*]. Los compuestos* **2** *disueltos en* CH_2Cl_2 *a 0 °C no reaccionan con exceso de CNtBu, pero sí lo hacen con CO (1 atm), dando lugar a la ruptura de los puentes y formación de una serie de carbonil-derivados terminales de* Ni^{II} *de fórmula Qcis-*$[Ni(C_6F_5)_2X(CO)]$ (**4**)*. Las frecuencias de tensión ν(CO) de los compuestos* **4** *disueltos en* CH_2Cl_2 *decrecen en el siguiente orden: Cl (2090 cm*$^{-1}$*) > Br (2084 cm*$^{-1}$*) > I (2073 cm*$^{-1}$*). Los derivados* **4** *regeneran sus correspondientes compuestos de partida,* **2***, cuando aumenta la temperatura o disminuye la presión de CO.* $[NBu_4]$*cis-*$[Ni(C_6F_5)_2Cl(CO)]$ (**4a**) *reacciona con* AgC_6F_5 *dando* $[NBu_4][Ni(C_6F_5)_3(CO)]$ (**5**, $\nu_{CO}(CH_2Cl_2) = 2070\ cm^{-1}$)*. El compuesto* **5** *también se forma cuantitativamente (*^{19}F *NMR) mediante reacción 1:1 de* **1** *con HCl(*Et_2O*) en atmósfera de CO. El compuesto* **3** *reacciona a –78 °C con CO dando cis-*$[Ni(C_6F_5)_2(CO)_2]$ (**6**, $\nu_{CO}(CH_2Cl_2) = 2156, 2130\ cm^{-1}$)*, que se descompone fácilmente mediante eliminación reductora de* $C_6F_5{-}C_6F_5$*. Tanto el compuesto* **3** *como* **6** *reaccionan con CNtBu dando trans-*$[Ni(C_6F_5)_2(CNtBu)_2]$ (**7**)*. Las estructuras en estado sólido de los compuestos* **3**, **4b**, **6** *y* **7** *han sido determinadas por difracción de rayos X. Los compuestos* **4**–**6** *constituyen raros ejemplos de carbonilos de* Ni^{II} *de geometría cuadrada plana.*

Results and Discussion

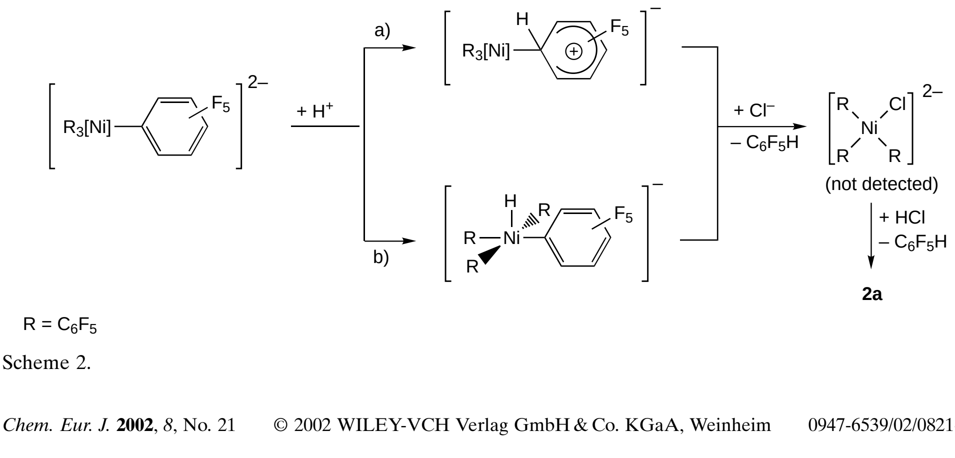
Synthesis of anionic pentafluorophenyl derivatives of nickel(II): The arylation of $[NBu_4]_2[NiBr_4]$ with LiC_6F_5 in 1:8 molar ratio gives $[NBu_4]_2[Ni(C_6F_5)_4]$ (**1**) as a yellow, air- and moisture-stable solid in 83 % yield. The preparation of **1** had been previously communicated by some of us, but no experimental details on the synthetic procedure were given in that report.[8] The IR spectrum of **1** contains a single sharp absorption at 759 cm^{-1} assignable to the X-sensitive vibration mode of the C_6F_5 group (Table 1).[9] This is, in principle, compatible with both tetrahedral (T_d, IR active Γ_{M-C} fundamentals: F_2) and square-planar (D_{4h}, IR active Γ_{M-C} fundamentals: E_u) metal environments.[10] The ^{19}F NMR spectrum of **1** contains well-defined signals corresponding to a single type of C_6F_5 groups (Table 2). Since tetrahedral Ni^{II} species (d^8) are expected to be paramagnetic,[11] compound **1** can be reasonably assigned a square-planar geometry.

Square-planar $[MR_4]^{2-}$ ions, in which M = Pd or Pt and R = C_6X_5 (X = F or Cl), are known to behave as Lewis bases[12] and are able to react with a number of Lewis acids including the most simple one: H^+. This has been attributed to the metal center bearing an excess of electron density, probably located in the d_{z^2} orbital.[12] The 1:2 reaction of a solution of **1** in CH_2Cl_2 with a solution of dry HCl(g) in Et_2O affords $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (**2a**) in quantitative spectroscopic yield (^{19}F NMR spectroscopy), together with the stoichiometrically required amount of C_6F_5H (Scheme 1). Following



Scheme 1.

the results obtained in protonation reactions on different organoplatinum(II) complexes,[13] it is sensible to suggest that the protonolysis of the Ni–C_6F_5 bonds in **1** can occur (Scheme 2) by a) direct attack of the solvated H^+ on the *ipso*-C atom, or b) through formation of transient Ni^{IV}–H intermediates as the result of a Lewis acid/base neutralization process, followed by reductive elimination of C_6F_5H. In either case, the reaction should result in the formation of $[Ni(C_6F_5)_3Cl]^{2-}$; this species, however, could not be spectroscopically detected. The 1:1 reaction of **1** with $HCl(Et_2O)$ only gives (^{19}F NMR spectroscopy) equimolar mixtures of **2a** and unreacted **1**, with no evidence for the formation of $[Ni(C_6F_5)_3Cl]^{2-}$. The fact that **1** undergoes a double protonolysis could be attributed to the Ni center being more basic in $[Ni(C_6F_5)_3Cl]^{2-}$ than in $[Ni(C_6F_5)_4]^{2-}$. This proposal would apparently be in contrast with the much weaker electron-withdrawing effect traditionally assigned to the C_6F_5 group with respect to single halogen atoms (F or Cl).[14] It must be remembered, however, that many of the properties of the perfluorophenylmetal derivatives "cannot be simply ascribed to a strong electron-withdrawing effect of the C_6F_5 ring but rather to the unusual π system that results from p–π interactions".[14a] It is an experimental fact that $[Ni(C_6F_5)_4]^{2-}$ and $[Pd(C_6F_5)_4]^{2-}$ react with HCl(solv) to give $[\{M(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]^{2-}$ as the result of a double protonolysis, while in the case of $[Pt(C_6F_5)_4]^{2-}$ the reaction proceeds stepwise, thus allowing the detection and even isolation of $[Pt(C_6F_5)_3Cl]^{2-}$ salts.[15] The different results obtained for the lighter and the heavy Group 10 metals could well be due to the different nature of the pπ–dπ M–L interaction in each case (M = Ni, Pd, Pt; L = Cl, C_6F_5).



Scheme 2.

The most relevant IR absorptions of **2a** (Table 1) are in good agreement with those reported for the salt $[NEt_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$, which had been obtained by reaction of $[Ni(C_6F_5)_2(\eta^6\text{-}PhMe)]$ with NEt_4Cl.[16] The ^{19}F NMR data are given in Table 2.

Synthesis of *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (3): Metal complexes that contain vacant coordination sites are highly desirable species for synthetic and catalytic purposes. Useful synthons for these commonly unstable species are adducts that contain weakly coordinated, labile ligands, as for instance some solvent complexes (solvates).[17]

The complex that we initially sought to prepare was based on an early report by Royo and co-workers: $[Ni(C_6F_5)_2(1,4\text{-}dioxane)_2]$.[18] The reaction of $NiBr_2$ with $Mg(C_6F_5)Br$ in THF, followed by addition of 1,4-dioxane to remove the magnesium dibromide ostensibly gave the 1,4-dioxane adduct of the "$Ni(C_6F_5)_2$" fragment based on elemental analysis exclusively. In our hands, however, an orange compound was obtained that eventually was characterized as $[Ni(C_6F_5)_2(thf)_2]$ (**3**) based on a single-crystal X-ray diffraction study and independent synthesis.

The 1:2 reaction of **2a** with $AgClO_4$ in THF affords *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (**3**) as an orange solid in 68% yield (Scheme 1). This synthetic procedure had already been successfully used to prepare the Pd and Pt homologues.[6, 19] The ^{19}F NMR data of **3** are given in Table 2. Its IR spectroscopic features (Table 1) are in good agreement with those given by Brezinski and Klabunde for *trans*-$[Ni(C_6F_5)_2(thf)_2]$.[20] This compound had been obtained with 41% yield by replacement of toluene in $[Ni(C_6F_5)_2(\eta^6\text{-}PhMe)]$ by THF.[21] The most significant IR data of the series of compounds *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Ni, Pd, and Pt) are given in Table 3 for comparison. As it appears there, the Pd and Pt compounds show two clearly defined IR absorptions assignable to the X-sensitive vibration modes of the C_6F_5 groups as expected for a *cis* arrangement of the ligands (C_{2v}, IR active $\Gamma_{M\text{-}C}$ fundamentals: $A_1 + B_1$). In complex **3**, however, the absorptions associated with these vibration modes seem to be so similar in energy that they overlap to give the experimentally observed broad band at 786 cm^{-1} with a shoulder at 796 cm^{-1}. The deceptively simple appearance of the X-sensitive band first suggested a *trans* geometry for this compound.[20]

A single-crystal X-ray diffraction study of **3** has revealed that the compound has in fact a *cis* geometry in keeping with the heavier metal homologues. Crystallographic data are given in Table 4 and selected interatomic distances and angles appear in Table 5. The structure of *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (**3**) is depicted in Figure 1. The geometry around Ni is best described as square planar. The sum of the bond angles defined by the atoms directly bonded to nickel, O(1S) and O(2S) of THF and C(11) and C(21) of C_6F_5,

Table 3. Important IR data [cm^{-1}] for the known members of the family of compounds $[MX_2L_2]$ (M = Ni, Pd, Pt; X = Cl, C_6F_5; L = CO, THF).

Compound	ν(CO)	ν(C–F)	X-sensitive
cis-$[Ni(C_6F_5)_2(thf)_2]$[a,b]	–	953	796 (sh), 786
cis-$[Pd(C_6F_5)_2(thf)_2]$[c]	–	954	802, 792
cis-$[Pt(C_6F_5)_2(thf)_2]$[d]	–	953	818, 806
trans-$[NiCl_2(CO)_2]$[e]	2148	–	–
cis-$[PtCl_2(CO)_2]$[f]	2190, 2152	–	–
trans-$[PtCl_2(CO)_2]$[g]	2150	–	–
cis-$[Ni(C_6F_5)_2(CO)_2]$[a]	2162, 2138	957	796 (sh), 788
cis-$[Pd(C_6F_5)_2(CO)_2]$[c]	2186, 2163	962	798, 786
cis-$[Pt(C_6F_5)_2(CO)_2]$[d]	2174, 2143	961	804, 792 (sh)
trans-$[Pt(C_6F_5)_2(CO)_2]$[d]	2151	964	790

[a] This work. [b] Ref. [20]. [c] Refs. [6] and [19b]. [d] Refs. [6] and [19]. [e] Ref. [4a]. [f] Ref. [42]. [g] Ref. [43].

equals 360.2°. The Ni–C_6F_5 bond lengths in **3** are identical (186.8(6) and 186.4(6) pm for Ni–C(11) and Ni–C(21), respectively) and belong to the lower end of Ni–C distances found in the pentafluorophenylnickel derivatives for which the X-ray crystal structure is known (mean Ni–C_6F_5 distance: 190.0 pm; min/max values: 186.6/194.0 pm).[22, 23] The two chemically independent C_6F_5 groups are tilted with respect to the Ni coordination plane (tilt angle of the C(11)–C(16) ring = 78.0°; tilt angle of the C(21)–C(26) ring = 74.4°). The Ni–O distances (195.3(4) and 195.5(4) pm) are similar to that found in $[Ni\{L_3\}(thf)]$ (Ni–O 196.6(1) pm; L_3 = PhNC(=NPh)N(Ph)CN(Ph)C(=NPh)NPh-$\kappa^2 N,\kappa C$), which is the only structurally characterized square-planar nickel compound containing the THF ligand;[24] the Ni–O bond distance found in this compound was considered too short by Hoberg and his co-workers and was attributed to an enhanced electronic demand of the "Ni{L_3}" carbene–nickel fragment. A longer Ni–O bond length (202.6(3) pm) was, in fact, found in $[\{NiCl_2(thf)\}(\mu\text{-}NC)\{Mn(CO)(dppm)_2\}]$, a heterodinuclear species with a highly distorted tetrahedral geometry around

Table 5. Selected bond lengths [pm] and angles [°] and their estimated standard deviations for **3**.

Ni–C(11)	186.8(6)	C(21)–C(22)	138.2(8)
Ni–C(21)	186.4(6)	C(21)–C(26)	136.3(8)
Ni–O(1S)	195.3(4)	C(22)–F(22)	135.3(7)
Ni–O(2S)	195.5(4)	C(26)–F(26)	135.3(7)
C(11)–C(12)	137.2(9)	O(1S)–C(1S)	140.4(8)
C(11)–C(16)	137.8(8)	O(1S)–C(4S)	141.8(8)
C(12)–F(12)	134.7(7)	O(2S)–C(5S)	143.2(7)
C(16)–F(16)	136.1(7)	O(2S)–C(8S)	141.2(8)
C(11)-Ni-C(21)	87.6(3)	Ni-C(21)-C(22)	122.0(6)
C(11)-Ni-O(1S)	93.8(2)	Ni-C(21)-C(26)	125.4(5)
C(11)-Ni-O(2S)	177.1(3)	C(22)-C(21)-C(26)	112.4(6)
C(21)-Ni-O(1S)	177.3(3)	C(21)-C(22)-F(22)	118.2(7)
C(21)-Ni-O(2S)	93.7(2)	C(21)-C(26)-F(26)	118.9(7)
O(1S)-Ni-O(2S)	85.1(2)	Ni-O(1S)-C(1S)	124.1(5)
Ni-C(11)-C(12)	121.4(5)	Ni-O(1S)-C(4S)	123.3(5)
Ni-C(11)-C(16)	125.1(5)	Ni-O(2S)-C(5S)	124.8(4)
C(12)-C(11)-C(16)	113.5(6)	Ni-O(2S)-C(8S)	123.6(5)
C(11)-C(12)-F(12)	119.8(6)	C(1S)-O(1S)-C(4S)	109.0(6)
C(11)-C(16)-F(16)	118.2(6)	C(8S)-O(2S)-C(5S)	108.6(5)

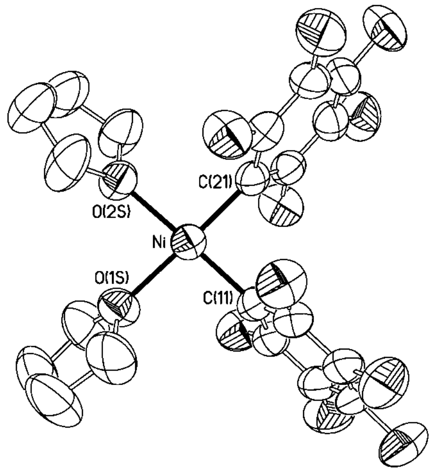


Figure 1. Thermal ellipsoid diagram (50% probability) of **3**.

Table 4. Crystal data and structure refinement for *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (**3**), $[PPh_3Me]$*cis*-$[Ni(C_6F_5)_2Br(CO)]$ (**4b**), *cis*-$[Ni(C_6F_5)_2(CO)_2]$ (**6**) and *trans*-$[Ni(C_6F_5)_2(CNtBu)_2]$ (**7**)

	3	**4b**	**6**	**7**
formula	$C_{20}H_{16}F_{10}NiO_2$	$C_{32}H_{18}BrF_{10}NiOP$	$C_{14}F_{10}O_2Ni$	$C_{22}H_{18}F_{10}N_2Ni$
a [pm]	2548.9(7)	1096.6(3)	1752.4(3)	1776.2(3)
b [pm]	2548.9(7)	1151.1(3)	8449.6(14)	1076.11(18)
c [pm]	1285.8(3)	1404.3(3)	9518.4(16)	1372.3(2)
α [°]	90	113.446(4)	90	90
β [°]	90	107.542(4)	90	116.661(3)
γ [°]	90	95.290(4)	90	90
V [nm^3], *Z*	8.354(4), 16	1.5044(6), 2	1.4094(4), 4	2.3440(7), 4
ρ_{calcd} [g cm^{-3}]	1.708	1.718	2.115	1.584
T [K]	293(2)	173(1)	100(1)	100(1)
crystal system	tetragonal	triclinic	orthorhombic	monoclinic
space group	$I4_1/a$	$P\bar{1}$	*Pbcn*	*C2/c*
dimensions [mm]	0.42 × 0.42 × 0.79	0.40 × 0.40 × 0.30	0.38 × 0.28 × 0.20	0.36 × 0.30 × 0.17
μ [mm^{-1}]	1.032	2.115	1.507	0.920
absorption correction	psi scans	1940 equiv reflns	3301 equiv reflns	1201 equiv reflns
2θ range [°]	3.20–45.88	4.0–50.0 ($\pm h$, $\pm k$, $\pm l$)	2.3–50.1 ($\pm h$, $\pm k$, $\pm l$)	4.6–50.0 ($\pm h$, $\pm k$, $\pm l$)
reflections collected	3020	8224	6171	6218
independent reflections	2863 (R_{int} = 0.026)	5178 (R_{int} = 0.0559)	1242 (R_{int} = 0.0368)	2073 (R_{int} = 0.0369)
final *R* indices [$I > 2\sigma(I)$][a]	$R1 = 0.0610$, $wR2 = 0.103$	$R1 = 0.0607$, $wR2 = 0.1448$	$R1 = 0.0298$, $wR2 = 0.0700$	$R1 = 0.0379$, $wR2 = 0.0645$
R indices (all data)	$R1 = 0.121$, $wR2 = 0.121$	$R1 = 0.0720$, $wR2 = 0.1496$	$R1 = 0.0377$, $wR2 = 0.0723$	$R1 = 0.0572$, $wR2 = 0.0681$
goodness-of-fit on F^2 [b]	1.024	1.006	0.991	0.983
Largest diff. peak/hole [e nm^{-3}]	234/ – 237	867/ – 667	459/ – 242	623/ – 419

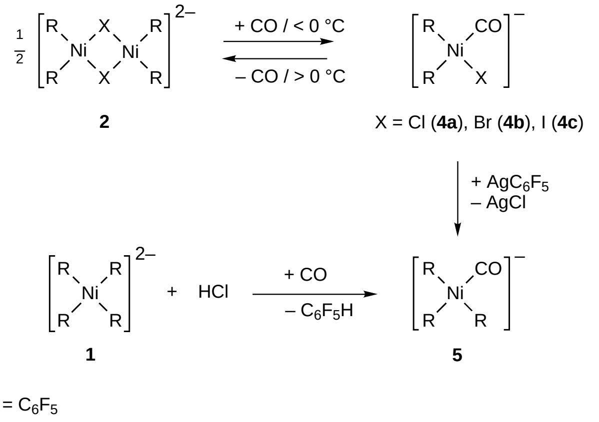
[a] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$; $R1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$. [b] Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/N_{obs} - N_{param}]^{0.5}$.

the Ni center.[25] All the other structurally characterized tetrahydrofuran–nickel compounds are six-coordinate with even longer Ni–O distances (mean value: 208.1 pm; min/max values: 203.7/212.7 pm).[26]

Synthesis of square-planar nickel(II) carbonyl derivatives

Anionic species: The THF molecules in complex **3** can be easily replaced by better ligands. Thus, the 1:1 reaction of **3** with phosphonium halides, $[PPh_3Me]X$, yield (Scheme 1) the halide-bridged dinuclear species $[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]$ (X = Br (**2b**) or I (**2c**)). These compounds have been identified by elemental analyses and by IR (Table 1) and ^{19}F NMR (Table 2) spectroscopy.

Reddish solutions of compounds **2** in CH_2Cl_2 at 0 °C rapidly turn yellow under a CO atmosphere. The solutions show single, sharp IR absorptions assignable to $\nu(CO)$ with the following values: Cl (2090 cm^{-1}) > Br (2084 cm^{-1}) > I (2073 cm^{-1}). These values compare well with the corresponding known Pt homologues *cis*-$[Pt(C_6F_5)_2X(CO)]^-$, for which the following $\nu(CO)$ values were observed in CH_2Cl_2: Cl (2091 cm^{-1}) > Br (2087 cm^{-1}).[19b] In view of the similar spectroscopic features observed for the Pt and Ni derivatives, it is sensible to assign the formula *cis*-$[Ni(C_6F_5)_2X(CO)]^-$ for the latter. The halide-bridge splitting effected by the CO molecule in compounds **2** is easily reversed when the temperature is allowed to rise or when the CO pressure is reduced (Scheme 3). Considering these limitations, the isolation of the complexes [Q]*cis*-$[Ni(C_6F_5)_2X(CO)]$ (QX = NBu_4Cl (**4a**), PPh_3MeBr (**4b**), and PPh_3MeI (**4c**)) as yellow solids is better achieved by precipitation from their solutions with CO-saturated *n*-hexane at −30 °C. The IR spectra of complexes **4** invariably show an absorption with an unresolved shoulder assignable to the X-sensitive vibration modes of the C_6F_5 groups (Table 1). This observation is compatible with both the *cis* (C_s, IR active Γ_{M-R} fundamentals: 2A′) and the *trans* (C_{2v}, IR active Γ_{M-R} fundamentals: $A_1 + B_1$) geometries. However, the presence of two sets of C_6F_5 signals in the ^{19}F NMR spectra (Table 2) strongly supports the *cis* formulation.



Scheme 3.

The solid-state structure of **4b** has been established by single-crystal X-ray diffraction analysis. Crystallographic data are given in Table 4 and selected interatomic distances and angles appear in Table 6. The structure of the anion *cis*-$[Ni(C_6F_5)_2Br(CO)]^-$ is depicted in Figure 2. The Ni atom is located in a nearly square-planar environment with angles between adjacent ligands ranging from 86.9(2)° to 91.91(15)°.

Table 6. Selected bond lengths [pm] and angles [°] and their estimated standard deviations for **4b**.

Ni–Br	233.7(1)	C(6)–F(6)	136.3(5)
Ni–C(1)	191.8(5)	C(7)–C(8)	136.9(7)
Ni–C(7)	191.5(5)	C(7)–C(12)	136.8(6)
Ni–C(13)	181.6(6)	C(8)–F(8)	136.0(5)
C(1)–C(2)	138.5(6)	C(12)–F(12)	136.2(5)
C(1)–C(6)	136.3(7)	C(13)–O	108.0(6)
C(2)–F(2)	134.8(6)		
Br-Ni-C(1)	91.30(13)	Ni-C(1)-C(6)	122.0(4)
Br-Ni-C(7)	178.19(13)	C(6)-C(1)-C(2)	114.9(4)
Br-Ni-C(13)	91.91(15)	Ni-C(7)-C(8)	122.5(4)
C(1)-Ni-C(7)	86.90(19)	Ni-C(7)-C(12)	122.5(4)
C(1)-Ni-C(13)	176.0(2)	C(12)-C(7)-C(8)	114.9(4)
C(7)-Ni-C(13)	89.9(2)	Ni-C(13)–O	178.2(4)
Ni-C(1)-C(2)	122.9(4)		

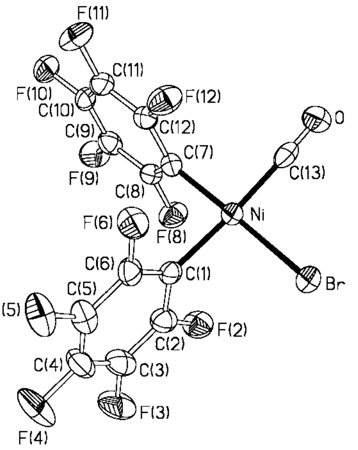


Figure 2. Thermal ellipsoid diagram (50 % probability) of the anion of **4b**.

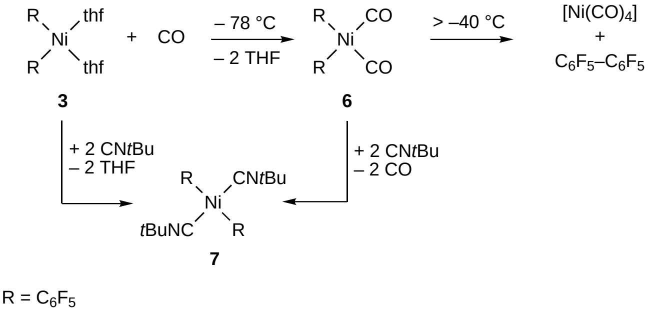
The two Ni–C_6F_5 distances are virtually identical (191.5(5) and 191.8(5) pm) and compare well with those found in other pentafluorophenyl nickel(II) derivatives structurally characterized (mean Ni–C_6F_5 distance: 190.0 pm).[22] The presumably different *trans* influence exerted by the Br^- and CO ligands has in this case no noticeable structural consequences.[27] The two chemically independent C_6F_5 groups are tilted with respect to the Ni coordination plane (tilt angle of the C(1)-C(6) ring = 78.9°; tilt angle of the C(7)-C(12) ring = 85.7°). The Ni–Br distance (233.7(1) pm) does not significantly deviate from the mean value found for terminal Ni–Br bonds in square-planar nickel compounds (235.2 pm).[28] The Ni-C(13)-O unit is practically linear (178.2(4)°) and the Ni–C(13) distance (181.6(6) pm) is significantly longer than that found in the square-planar Ni^{II} carbonyl compound $[N(PPh_3)_2][Ni(SePh)_3(CO)]$ (Ni–C = 172.9(8) pm).[29, 30] A handful of five-coordinate carbonyl nickel(II) derivatives have been structurally characterized with experimental Ni–CO distances ranging from 172.8(23) pm in (*TBPY*-5-22)-$[NiI_2$-

$(CO)(PMe_3)_2]$[31] to 181.7(16) pm in (*TBPY*-5-23)-$[NiI_2(CO)(fdma)]$ (fdma = ferrocene-1,1′-bis(dimethylarsine)).[32] As far as we know, this considerable difference could not be rationalized in terms of simple parameters such as the coordination site occupied by the CO ligand (axial or equatorial) and the global charge of the complex (going from 2+ to 2−). No correlation between the Ni–CO distance and the ν(CO) frequency seem to be apparent either (see below).

The ease with which complexes **4** release CO, spontaneously reverting to their respective parent compounds **2** is due to the presence of terminal halo ligands. These X^- ligands (X = Cl, Br, I), which are able to act as efficient nucleophiles, effect the intermolecular CO substitution. This decomposition pathway can be hindered by replacing the X^- ligand in **4** by another anionic ligand with poor nucleophilic character, such as C_6F_5. The reaction of in situ generated solutions of **2a** with AgC_6F_5 proceeds with replacement of the chloro ligand by the C_6F_5 group giving rise to $[NBu_4][Ni(C_6F_5)_3(CO)]$ (**5**), which can be isolated as a yellow solid in 51 % yield (Scheme 3). The ν(CO) vibration appears both in solution ($\nu_{CO}(CH_2Cl_2) = 2070\ cm^{-1}$) and in the solid state ($\nu_{CO}(KBr) = 2065\ cm^{-1}$; Table 1) at slightly lower frequencies than observed for any of the halide analogues **4**. The ^{19}F NMR spectrum of **5** (Table 2) shows two sets of C_6F_5 signals in 1:2 integrated ratio with the *o*-F signals of both sets being isochronous.

Complex **5** also forms by 1:1 reaction of **1** with $HCl(Et_2O)$ under a CO atmosphere (Scheme 3). This method is of little synthetic use because **5** cannot be satisfactorily freed from the NBu_4Cl thereby formed. However, it is interesting to compare this result with that obtained when **1** is treated with $HCl(Et_2O)$ in the absence of CO. In this case, we have attributed the failure to detect the intermediate species $[Ni(C_6F_5)_3Cl]^{2-}$ to the enhanced basicity of the Ni center in comparison with the parent species $[Ni(C_6F_5)_4]^{2-}$ (see above). Since the CO molecule is a good π-acceptor, poor σ-donor neutral ligand, the Lewis basicity of the Ni center in $[Ni(C_6F_5)_3(CO)]^-$ would be expected to be significantly lower than in $[Ni(C_6F_5)_3Cl]^{2-}$ or in $[Ni(C_6F_5)_4]^{2-}$. The fact that the reaction of **1** with $HCl(Et_2O)$ under CO atmosphere stops at the first stage, that is, $[Ni(C_6F_5)_3(CO)]^-$, lends further support to the protonolysis proceeding through the intermediacy of Ni^{IV}–H species. Another interesting feature of this reaction is that, after the elimination of C_6F_5H, the "$Ni(C_6F_5)_3$" fragment binds preferentially CO with formation of $[Ni(C_6F_5)_3(CO)]^-$ even in the presence of Cl^- ions.

Synthesis of cis-*$[Ni(C_6F_5)_2(CO)_2]$ (**6**)*: The solvent complexes *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd, Pt) are known to react with CO yielding the dicarbonyl derivatives *cis*-$[M(C_6F_5)_2(CO)_2]$ as the result of a simple ligand replacement process.[6, 19] We have now observed that solutions of **3** in CH_2Cl_2 react with CO at −78 °C in a similar way (Scheme 4) giving rise to *cis*-$[Ni(C_6F_5)_2(CO)_2]$ (**6**, $\nu_{CO}(CH_2Cl_2) = 2156,\ 2130\ cm^{-1}$). Even at that temperature the reaction takes place quite rapidly as evidenced by the color of the solution changing from orange to yellow. Compound **6** can be isolated from these solutions as a yellow solid if all the required operations are carried out at −78 °C. Otherwise it readily decomposes in the solid state and especially in solution, suffering reductive elimination of C_6F_5–C_6F_5 and concomitant formation of $[Ni(CO)_4]$ (Scheme 4). This decomposition path is in agreement with previous reports on the reactivity of $[Ni(C_6F_5)_2(\eta^6\text{-}PhMe)]$ with CO at room temperature[21] or at 0 °C.[33] The IR data of **6** are given in Table 1 and compared with those of the heavier metal homologues *cis*-$[M(C_6F_5)_2(CO)_2]$ (M = Pd, Pt) in Table 3. All these compounds show two ν(CO) IR absorptions of nearly equal intensity, assignable to the symmetric and asymmetric stretching vibrations expected for a *cis* geometry (C_{2v}, IR active Γ_{CO} fundamentals: $A_1 + B_1$). In all three cases, the absorption assignable to the symmetric $\nu(CO)_2$ vibration appears at higher frequencies than for free CO ($\nu(CO) = 2143\ cm^{-1}$).[34] This is consistent with the CO molecule acting as mainly a σ-donor ligand. The ν(CO) frequencies in *cis*-$[M(C_6F_5)_2(CO)_2]$ decrease in the order Pd > Pt > Ni, while the sequence of stability is as follows Pt > Pd > Ni. The nickel dicarbonyl compound occupies an unfavorable position probably because of the high stability of $[Ni(CO)_4]$, which could act as a driving force for the reductive elimination reaction.



Scheme 4.

The solid-state structure of **6** has been established by low-temperature single-crystal X-ray diffraction analysis. Crystallographic data are given in Table 4 and selected interatomic distances and angles appear in Table 7. The structure of the neutral species *cis*-$[Ni(C_6F_5)_2(CO)_2]$ (**6**) is depicted in Figure 3. The molecule has a crystallographically imposed C_2 axis bisecting the $Ni(C_6F_5)_2$ and $Ni(CO)_2$ angles. The only crystallographically independent Ni–C_6F_5 distance (Ni–C(1) = 191.9(2) pm) is similar to those found in **4b** in spite of their

Table 7. Selected bond lengths [pm] and angles [°] and their estimated standard deviations for **6**.

Ni–C(1)	191.9(2)	C(5)–C(6)	137.6(3)
Ni–C(7)	184.0(3)	F(2)–C(2)	136.4(3)
C(1)–C(2)	137.0(3)	F(3)–C(3)	134.6(3)
C(1)–C(6)	137.6(3)	F(4)–C(4)	133.6(3)
C(2)–C(3)	137.0(3)	F(5)–C(5)	134.1(3)
C(3)–C(4)	137.2(3)	F(6)–C(6)	135.5(3)
C(4)–C(5)	137.4(4)	C(7)–O	110.8(3)
C(1)-Ni-C(1′)	85.84(14)	C(1)-C(2)-C(3)	123.4(2)
C(1)-Ni-C(7)	174.78(11)	C(1)-C(6)-C(5)	123.1(2)
C(1)-Ni-C(7′)	89.04(10)	C(1)-C(2)-F(2)	119.7(2)
C(7)-Ni-C(7′)	96.10(16)	C(2)-C(3)-C(4)	119.3(2)
Ni-C(7)-O	179.6(2)	C(3)-C(4)-C(5)	119.5(2)
Ni-C(1)-C(2)	124.20(19)	C(4)-C(5)-C(6)	119.1(2)
Ni-C(1)-C(6)	120.25(18)	C(1)-C(6)-F(6)	119.4(2)
C(2)-C(1)-C(6)	115.5(2)		

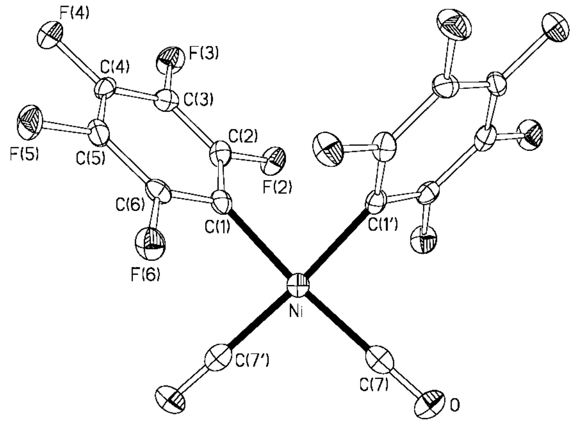


Figure 3. Thermal ellipsoid diagram (50 % probability) of **6**.

different global charge (see above). The C_6F_5 group is tilted 66.4° with respect to the Ni coordination plane. It is interesting to note that the C-Ni-C angle involving the *cis* CO ligands (96.10(16)°) is about 10° wider than that involving the much more space-demanding C_6F_5 groups (85.84(14)°). The Ni-C(7)-O unit is virtually linear (179.6(2)°). The Ni−CO distance (Ni−C(7) = 184.0(3) pm) is slightly but not significantly longer than that found in **4b**. Similar Ni−CO distances had been reported for the neutral five-coordinate compound (*TBPY*-5-11)-$[Ni(SiCl_3)_2(CO)_3]$ (average Ni−C = 180(1) pm).[35]

Much interest has been focused on the study of Ni^{II} carbonyl complexes during the last decade, mainly because of its relevance to the nickel site in [FeNi] CO dehydrogenases.[36] As a result, a fair number of Ni^{II} carbonyl complexes have been prepared. Most of these complexes are five-coordinate, an observation that has been theoretically justified in terms of a more efficient π back-donation from the Ni^{II} center to the CO ligand.[37] In fact, five-coordinate nickel monocarbonyl derivatives containing the CO ligand in either axial or equatorial positions, show low-frequency ν(CO) values as for instance in (*TBPY*-5-23)-$[NiI_2(CO)(fdma)]$ (fdma = ferrocene-1,1′-bis(dimethylarsine); ν(CO) = 2054 cm^{-1}),[38] (*TBPY*-5-22)-$[NiI_2(CO)(PMe_3)_2]$ (ν(CO) = 2015 cm^{-1})[31] and (*TBPY*-5-13)-$[Ni(PP_3E)(CO)]^{2+}$ (PP_3E = tris{2-(diethylphosphino)ethyl}phosphine; ν(CO) = 2050 cm^{-1}).[39] Even in the tricarbonyl derivative (*TBPY*-5-11)-$[Ni(SiCl_3)_2(CO)_3]$, the ν(CO) absorption appears at 2079 cm^{-1}.[33] In a square-planar geometry, the σ-nonbonding $Ni(d_\pi)$ orbitals have been calculated to be low in energy and thus to be inefficient π-donor orbitals.[37] This statement, however, should be taken with great care, since in the anionic compounds **4** and **5** as well as in the few square-planar precedents reported, the ν(CO) values observed suggest a significant degree of π back-donation, see: *trans*-$[Ni(C_6Cl_5)(PR_3)_2(CO)]^+$ (PR_3 = $PPhMe_2$, PPh_2Me; ν(CO) = 2100 cm^{-1})[40] and $[Ni(SePh)_{3-x}(SPh)_x(CO)]^-$ (x = 0, 1, 2; ν(CO) ~ 2030 cm^{-1}).[29, 30] No structural proposal has been put forward for the dicarbonyl derivative $[Ni(F_2SiC(tBu){=}CHSiF_2\text{-}\kappa^2Si)(CO)_2]$ (ν(CO) = 2090 and 2040 cm^{-1}).[41] To the best of our knowledge, the ν(CO) values observed for *cis*-$[Ni(C_6F_5)_2(CO)_2]$ are the highest reported for any isolated nickel carbonyl derivative. The ν(CO) frequencies found in the simple dicarbonyl species *trans*-$[NiCl_2(CO)_2]$,[4a] *cis*-$[PtCl_2(CO)_2]$,[42] and *trans*-$[PtCl_2(CO)_2]$[43] are also given in Table 3 for comparison. The low-pressure (0.3 – 3.5 Pa), low-temperature (77 K) adsorption of CO on Ni^{II}/SiO_2 materials pretreated at 973 K has been recently reported to give rise to an IR band at 2201 cm^{-1}, which has been attributed to a four-coordinate Ni^{II} monocarbonyl species.[44] On the basis of its spectroscopic properties, the real species has been modeled by DFT calculations as $[Ni^{II}(OSiH_3)\{O(SiH_3)_2\}_2(CO)]^+$, whereby the $[Si_5O_3H_{15}]^-$ cluster was used as an acceptable simplification of the structurally complex silica surface.

The case of the CN*t*Bu ligand: In contrast to the results obtained with CO, the CN*t*Bu ligand is not able to split the bridging system in the dinuclear complexes **2**: the reaction of **2** with CN*t*Bu at 0 °C gives no sign (IR, NMR spectroscopy) for the formation of any new species. On the other hand, the reaction of **3** with excess CN*t*Bu proceeds with THF substitution yielding *trans*-$[Ni(C_6F_5)_2(CNtBu)_2]$ (**7**), which can be isolated as a yellow solid (Scheme 4). Complex **7** also forms by 2:1 reaction of **6** with CN*t*Bu at − 78 °C (Scheme 4). The solid-state IR spectrum of **7** (Table 1) shows a single sharp absorption at 2209 cm^{-1} assignable to the ν(C≡N), thus suggesting a *trans* geometry (D_{2h}, IR active Γ_{CN} fundamentals: B_{1u}). Accordingly, a single sharp absorption is also observed at 776 cm^{-1} assignable to the only IR active X-sensitive vibration mode of the C_6F_5 groups (B_{1u}). The solid-state structure of **7** has been established by single-crystal X-ray diffraction studies. Crystallographic data are given in Table 4 and selected interatomic distances and angles are gathered in Table 8. A drawing of the molecule is depicted in Figure 4. The Ni atom is located on an inversion center and its coordination environment is almost square planar with angles between adjacent donor atoms of 88.11(11)° and 91.89(11)°. The angles between the *trans* ligands are 180° as imposed by the crystal symmetry. The Ni−C_6F_5 distance (193.9(3) pm) is slightly but not significantly longer than those found in **4b** and **6**, belonging to the upper end of Ni−C distances found in the pentafluorophenylnickel derivatives for which the X-ray crystal structure has been reported (min/max values: 186.6/

Table 8. Selected bond lengths [pm] and angles [°] and their estimated standard deviations for **7**.

Ni−C(1)	193.9(3)	C(5)−C(6)	137.1(4)
Ni−C(7)	182.5(3)	C(2)−F(2)	136.4(3)
C(7)−N	114.6(3)	C(3)−F(3)	134.7(3)
N−C(8)	146.1(3)	C(4)−F(4)	134.8(3)
C(1)−C(2)	137.7(3)	C(5)−F(5)	134.9(3)
C(1)−C(6)	137.9(3)	C(6)−F(6)	136.0(3)
C(2)−C(3)	136.9(4)	C(8)−C(9)	151.4(4)
C(3)−C(4)	137.2(4)	C(8)−C(10)	151.4(4)
C(4)−C(5)	136.5(4)	C(8)−C(11)	152.2(3)
C(1)-Ni-C(7)	91.89(11)	C(2)-C(3)-C(4)	118.9(3)
C(1)-Ni-C(7′)	88.11(11)	C(3)-C(4)-C(5)	119.3(3)
Ni-C(7)-N	176.7(2)	C(4)-C(5)-C(6)	119.5(3)
C(7)-N-C(8)	174.2(3)	C(5)-C(6)-C(1)	124.1(3)
Ni-C(1)-C(2)	124.1(2)	N-C(8)-C(9)	107.3(2)
Ni-C(1)-C(6)	122.1(2)	N-C(8)-C(10)	106.7(2)
C(2)-C(1)-C(6)	113.6(2)	N-C(8)-C(11)	107.4(2)
C(1)-C(2)-F(2)	119.0(2)	C(9)-C(8)-C(10)	112.5(2)
C(1)-C(6)-F(6)	119.5(2)	C(9)-C(8)-C(11)	111.7(2)
C(1)-C(2)-C(3)	124.6(3)	C(10)-C(8)-C(11)	111.0(2)

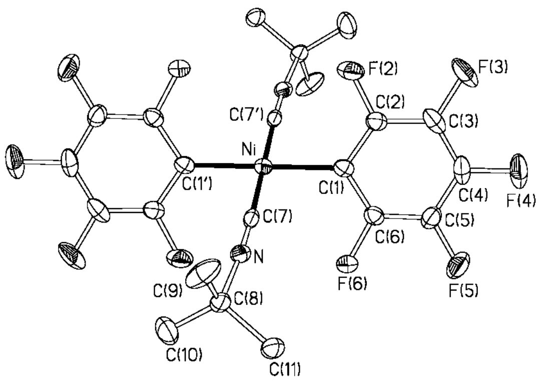


Figure 4. Thermal ellipsoid diagram (50% probability) of **7**.

194.0 pm).[22] The Ni–C distance in **7** is identical to that found in *trans*-$[Ni(C_6F_5)_2(PPh_2Me)_2]$ (Ni–C = 193.9(3) pm),[45] the whole geometry of the $Ni(C_6F_5)_2$ unit being very similar in both compounds. Thus, in both cases are the C_6F_5 rings eclipsed with shortest interannular $F\cdots F$ distances of about 412 pm. However, the C_6F_5 rings in **7** are markedly tilted with respect to the Ni coordination plane (tilt angle = 59.0°), while in *trans*-$[Ni(C_6F_5)_2(PPh_2Me)_2]$ they are almost perpendicular (tilt angle = 86.13°). The Ni–C≡N unit is almost linear (176.7(2)°) and the Ni–CN*t*Bu bond length (182.5(3) pm) compares well with those found in other square-planar Ni^{II} derivatives containing isocyanide ligands (Ni–CNR mean value: 184.5 pm).[46] The *t*Bu groups are staggered when projected along the C–N≡C–Ni–C≡N–C axis, as required by the presence of an inversion center on the Ni atom.

It is interesting to note that while the replacement of THF in **3** by CO takes place with retention of the metal-core geometry, the reaction of **3** with CN*t*Bu implies *cis*/*trans* isomerization giving the *trans* isomer as the stable solid-state species (IR spectroscopy, X-ray diffraction). However, the ^{19}F NMR spectrum of **7** in [^{2}H]chloroform at room temperature shows two sets of C_6F_5 signals in 3:2 integrated ratio. We assign these signals to the *cis* and *trans* isomers coexisting in solution. Accordingly, the IR spectrum of **7** in CH_2Cl_2 solution shows a broad band at 2197 cm^{-1} together with an unresolved shoulder at 2211 cm^{-1} in contrast to the single sharp ν(C≡N) absorption observed at 2209 cm^{-1} for solid samples of **7** (Table 1).

Conclusion

The anionic compound $[Ni(C_6F_5)_4]^{2-}$ (**1**) has proven a suitable starting material for a convenient entry to the chemistry of square-planar nickel(II) carbonyl compounds.

The halide-bridged dinuclear species $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}X)_2]^{2-}$ (X = Cl (**2a**), Br (**2b**), I (**2c**)) reversibly bind CO giving rise to the isolable derivatives *cis*-$[Ni(C_6F_5)_2X(CO)]^-$ (**4**). No reduction has been detected to occur during these reversible processes.

With the synthesis of *cis*-$[Ni(C_6F_5)_2(CO)_2]$ we have prepared an unprecedented family of isolable dicarbonyl compounds for all three Group 10 metals. The fact that the order of ν(CO) values within this family (Pd > Pt > Ni) does not parallel the order of stability (Pt > Pd > Ni) further evidences that the idea relating the degree of π back-bonding to the stability of a carbonyl compound is insufficient.

The isolation of complexes **4**–**7** has been possible because of the reluctance of M–C_6F_5 bonds to undergo insertion reactions. This can be considered a fortunate feature in this case, since, according to very recent results, the energy barrier associated with the CO insertion into Ni–CH_3 bonds is extremely low.[47]

Experimental Section

General procedures and materials: Unless otherwise stated, the reactions and manipulations were carried out under purified argon using Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The organolithium reagent LiC_6F_5[48] was prepared as described elsewhere. $HCl(Et_2O)$ was prepared by passing a slow stream of dry HCl(g) through Et_2O in an ice-bath; the solutions were acid/base titrated before use. Elemental analyses were carried out with a Perkin–Elmer 2400-Series II microanalyzer. IR spectra of KBr discs or CH_2Cl_2 solutions were recorded on the following Perkin–Elmer spectrophotometers: 883 (4000–200 cm^{-1}) or Spectrum One (4000–350 cm^{-1}). NMR spectra were recorded on a Varian Unity-300 spectrometer.

Synthesis of $[NBu_4]_2[NiBr_4]$: This synthetic procedure is based on the method given to prepare $[NEt_4]_2[NiBr_4]$.[49] A green solution of commercially available $NiBr_2\cdot xH_2O$ (Acros Organics, 18.8 mmol) in EtOH (30 cm^3) was added to NBu_4Br (9.6 g, 29.9 mmol) dissolved in EtOH (20 cm^3) and the mixture was refluxed for 1 min. The solvent was evaporated to about one half of the initial volume. After the addition of *i*PrOH (40 cm^3), the remaining EtOH was distilled. Allowing the resulting blue solution to stand at −30 °C overnight gave a blue solid which was filtered, washed with portions of *i*PrOH (3 × 5 cm^3) and Et_2O (2 × 5 cm^3) and vacuum dried (15.1 g, 17.5 mmol, 93% yield).

Synthesis of $[NBu_4]_2[Ni(C_6F_5)_4]$ (1): $[NBu_4]_2[NiBr_4]$ (3.0 g, 3.5 mmol) was added to a solution of LiC_6F_5 (ca. 27.8 mmol) in Et_2O (80 cm^3) at −78 °C. The suspension was allowed to warm to room temperature and stirred overnight. The resulting yellow solid was then filtered, washed with portions of H_2O (3 × 40 cm^3), EtOH (2 × 25 cm^3), and Et_2O (2 × 20 cm^3), and dried. Recrystallization in CH_2Cl_2/*i*PrOH gave **1** as a yellow solid in 83% yield (3.5 g, 2.9 mmol). Elemental analysis calcd (%) for $C_{56}H_{72}F_{20}N_2Ni$: C 55.5, H 6.0, N 2.3; found: C 55.3, H 5.9, N 2.5.

Synthesis of $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (2a): The dropwise addition of $HCl(Et_2O)$ (5.0 mmol) to a refluxing solution of **1** (3.0 g, 2.5 mmol) in CH_2Cl_2 (60 cm^3) causes the initially yellow solution to turn dark red. After refluxing for 2 h, the solution was evaporated to dryness. Treating the resulting reddish residue with *i*PrOH (30 cm^3) produced a red solid that was filtered, washed with Et_2O (2 × 5 cm^3), and vacuum dried (**2a**, 1.41 g, 1.05 mmol, 85% yield). Elemental analysis calcd (%) for $C_{56}H_{72}Cl_2F_{20}N_2Ni_2$: C 50.1, H 5.4, N 2.1; found: C 50.1, H 5.6, N 2.2.

Synthesis of $[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}Br)_2]$ (2b): Addition of $[PPh_3Me]Br$ (0.20 g, 0.56 mmol) to a solution of **3** (0.25 g, 0.46 mmol) in CH_2Cl_2 (25 cm^3) at 0 °C caused the color to change from orange to pink. After 1 h of stirring, the solution was concentrated to dryness. Treatment of the resulting residue with *i*PrOH (10 cm^3) produced a pink solid, which was filtered, washed with Et_2O (4 cm^3), and vacuum dried (**2b**, 0.14 g, 0.09 mmol, 40% yield). Elemental analysis calcd (%) for $C_{62}H_{36}Br_2F_{20}Ni_2P_2$: C 49.6, H 2.4; found: C 49.3, H 2.2.

Synthesis of $[PPh_3Me]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}I)_2]$ (2c): By using the procedure described for synthesis of **2b**, compound **2c** was prepared starting from **3** (0.27 g, 0.51 mmol) and $[PPh_3Me]I$ (0.24 g, 0.61 mmol). Complex **2c** was obtained as a pink solid (0.14 g, 0.09 mmol, 35% yield). Elemental analysis calcd (%) for $C_{62}H_{36}F_{20}I_2Ni_2P_2$: C 46.7, H 2.3; found: C 46.7, H 2.6.

Synthesis of *cis*-$[Ni(C_6F_5)_2(thf)_2]$ (3)

Method A: C_6F_5Br (12.9 g, 52.2 mmol) was added slowly through an addition funnel to a suspension of magnesium turnings in THF (50 cm^3) in a flask equipped with a reflux condenser. Within 5 min the surface of the magnesium became dull and the THF began to reflux. C_6F_5Br was added over 2 h. After about 1 h, the reaction mixture was added to a Kjeldahl flask containing a slurry of $NiBr_2$ (5.03 g, 23.2 mmol) in THF (25 cm^3). The mixture was heated to reflux for 3 h. A red solution resulted. 1,4-Dioxane (25 cm^3) was added to the solution. The solution turned brick orange and a precipitate formed. The mixture was stored at −20°C overnight. The flask was then allowed to warm to room temperature and the mixture was filtered to remove a gray solid. The solid was washed with 1,4-dioxane (20 cm^3). The filtrate was then stored again at −20 °C overnight. Orange crystals were collected by filtration and dried in vacuo. Yield 3.00 g (24 %); ^1H NMR ($CDCl_3$): $\delta = 3.67$ (s, 8H), 1.72 (s, 8H).

Method B: $AgClO_4$ (0.31 g, 1.48 mmol) was added to a solution of **2a** (1.00 g, 0.74 mmol) in THF (40 cm^3) at 0 °C and the mixture stirred for 45 min in the dark. The solvent was then evaporated to dryness, and the resulting residue extracted into Et_2O (160 cm^3) and filtered. The orange extract was evaporated to dryness. The residue was washed with *n*-hexane to give an orange solid which was filtered and vacuum dried (**3**, 0.54 g, 1.00 mmol, 68 % yield). Elemental analysis calcd (%) for $C_{20}H_{16}F_{10}NiO_2$: C 44.7, H 3.0; found: C 43.5, H 3.3. Crystals suitable for X-ray diffraction obtained by using Method A, were grown from 1,4-dioxane/THF solution.

Synthesis of [NBu_4]*cis*-[$Ni(C_6F_5)_2Cl(CO)$] (4a): A solution of **2a** (0.27 g, 0.20 mmol) in CH_2Cl_2 (25 cm^3) at 0 °C was allowed to react with CO for 30 min. The color of the solution gradually changed from red to yellow. Then, CO-saturated *n*-hexane (50 cm^3) was added and the mixture was allowed to stand at −30 °C overnight causing the precipitation of a yellow solid, which was filtered at −20 °C and vacuum dried at the same temperature (**4a**, 0.17 g, 0.24 mmol, 61 % yield). Elemental analysis calcd (%) for $C_{29}H_{36}ClF_{10}NNiO$: C 49.8, H 5.2, N 2.0; found: C 49.5, H 5.3, N 2.15.

Synthesis of [PPh_3Me]*cis*-[$Ni(C_6F_5)_2Br(CO)$] (4b): Compound **4b** was prepared from **2b** (0.15 g, 0.19 mmol) by using the procedure described for the synthesis of **4a**. Complex **4b** was obtained as a yellow solid (0.20 g, 0.25 mmol, 65 % yield). Elemental analysis calcd (%) for $C_{32}H_{18}BrF_{10}NiOP$: C 49.4, H 2.3; found: C 49.1, H 2.2. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (20 cm^3) into a solution of 25 mg of **4b** in CH_2Cl_2 (5 cm^3) at −78 °C.

Synthesis of [PPh_3Me]*cis*-[$Ni(C_6F_5)_2I(CO)$] (4c): Compound **4c** was prepared from **2c** (0.48 g, 0.30 mmol) by using the procedure described for the synthesis of **4a**. Complex **4c** was obtained as a yellow solid (0.18 g, 0.22 mmol, 36 % yield). Elemental analysis calcd (%) for $C_{32}H_{18}F_{10}INiOP$: C 46.6, H 2.2; found: C 46.7, H 2.6.

Synthesis of [NBu_4][$Ni(C_6F_5)_3(CO)$] (5): A solution of **2a** (0.51 g, 0.38 mmol) in CH_2Cl_2 (25 cm^3) at 0 °C was allowed to react with CO for 30 min, during which time, the color of the solution changed from red to yellow. This in situ prepared solution of **4a** was treated with AgC_6F_5[50] (0.21 g, 0.76 mmol) over a period of 30 min in the dark. The suspension obtained was filtered and the filtrate was concentrated almost to dryness. Then, *n*-hexane (15 cm^3) was added and the mixture was allowed to stand at −30 °C overnight causing the precipitation of a yellow solid, which was filtered and vacuum dried (**5**, 0.32 g, 0.38 mmol, 51 % yield). Elemental analysis calcd (%) for $C_{35}H_{36}F_{15}NNiO$: C 50.6, H 4.4, N 1.7; found: C 49.8, H 4.9, N 2.5.

Synthesis of *cis*-[$Ni(C_6F_5)_2(CO)_2$] (6): A solution of **3** (0.34 g, 0.64 mmol) in CH_2Cl_2 (20 cm^3) at −78 °C was allowed to react with CO over 3 h. The color of the solution first changed from orange to yellow and then a yellow solid formed; this solid was filtered at −78 °C and vacuum dried at the same temperature. Due to its high instability, no satisfactory elemental analyses could be obtained for **6**. Crystals suitable for X-ray diffraction analysis formed by allowing to stand a sealed tube containing a solution of **3** (0.21 g, 0.38 mmol) in CH_2Cl_2 (40 cm^3) in a CO atmosphere at −78 °C.

Synthesis of *trans*-[$Ni(C_6F_5)_2(CN$*t*$Bu)_2$] (7): The addition of CN*t*Bu (0.15 cm^3, 1.28 mmol) to a solution of **3** (0.28 g, 0.51 mmol) in CH_2Cl_2 (15 cm^3) at 0 °C caused the color to change from orange to yellow. After 1 h of stirring, *n*-hexane (60 cm^3) was added and the mixture was allowed to stand at −78 °C overnight causing the precipitation of a yellow solid, which was filtered and vacuum dried (**7**, 0.16 g, 0.29 mmol, 56 % yield). Elemental analysis calcd (%) for $C_{22}H_{18}F_{10}N_2Ni$: C 47.3, H 3.2, N 5.0; found: C 46.4, H 3.95, N 5.8. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (20 cm^3) into a solution of **7** (20 mg) in CH_2Cl_2 (5 cm^3) at −78 °C.

X-ray structure determinations: Crystal data and other details of the structure analyses are presented in Table 4. Suitable crystals of **3**, **4b**, **6** and **7** were obtained as indicated in each synthetic procedure. Crystals were mounted at the end of a glass fiber. The radiation used in all cases was graphite monochromated $Mo_{K\alpha}$ ($\lambda = 71.073$ pm).

Data for 3: Unit cell dimensions were determined by using 15 centered reflections. An absorption correction was applied on the basis of six ψ scans (max/min relative transmission factors: 0.871/1.000). Reflections were collected on a Syntex $P2_1$ diffractometer by using full (1.20°-wide) ω scans.

Data for 4b: Unit cell dimensions were initially determined from the positions of 149 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions for 786 reflections from the main data set. A hemisphere of data was collected on a Bruker SMART APEX diffractometer based on three ω-scan runs (starting $\omega = -28°$) at values $\phi = 0$, 90, and 180° with the detector at $2\theta = 28°$. For each of these runs, frames (606) were collected at 0.3° intervals and 10 s per frame. An absorption correction was applied on the basis of 3687 symmetry equivalent reflection intensities (max/min transmission factors: 1.000/0.493).

Data for 6: Unit cell dimensions were initially determined from the positions of 98 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions for 892 reflections from the main data set. A hemisphere of data was collected on a Bruker SMART APEX diffractometer based on three ω-scan runs (starting $\omega = -28°$) at values $\phi = 0$, 90, and 180° with the detector at $2\theta = 28°$. For each of these runs, frames (435) were collected at 0.3° intervals and 10 s per frame. An absorption correction was applied on the basis of 3301 symmetry equivalent reflection intensities (max/min transmission factors: 1.000/0.479).

Data for 7: Unit cell dimensions were initially determined from the positions of 74 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions for 682 reflections from the main data set. A hemisphere of data was collected on a Bruker SMART APEX diffractometer based on three ω-scans runs (starting $\omega = -28°$) at values $\phi = 0$, 90, and 180° with the detector at $2\theta = 28°$. For each of these runs, frames (230) were collected at 0.3° intervals and 10 s per frame. An absorption correction was applied on the basis of 2818 symmetry equivalent reflection intensities (max/min transmission factors: 1.000/0.853).

The structures were solved by Patterson and Fourier methods. All refinements were carried out by using the program SHELXL-97.[51] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon atoms (1.5 times for methyl hydrogen atoms). Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 4. Lorentz and polarization corrections were applied for all the structures.

CCDC-187756, CCDC-187757, CCDC-187758, and CCDC-187759 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre , 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

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[1] L. Mond, C. Langer, F. Quincke, *J. Chem. Soc.* **1890**, 749.

[2] a) E. P. Kündig, D. McIntosh, M. Moskovits, G. A. Ozin, *J. Am. Chem. Soc.* **1973**, *95*, 7234; b) P. Kündig, M. Moskovits, G. A. Ozin, *Can. J. Chem.* **1972**, *50*, 3587.

[3] P. Schützenberger, *Bull. Soc. Chim. Fr.* **1868**, *10*, 188.

[4] a) L. Shao, L. Zhang, M. Zhou, Q. Qin, *Organometallics* **2001**, *20*, 1137; b) I. R. Beattie, P. J. Jones, N. A. Young, *J. Am. Chem. Soc.* **1992**, *114*, 6146; c) D. A. van Leirsburg, C. W. DeKock, *J. Phys. Chem.* **1974**, *78*, 134; d) C. W. DeKock, D. A. van Leirsburg, *J. Am. Chem. Soc.* **1972**, *94*, 3235.

[5] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 91st–100th ed., de Gruyter, Berlin, **1985**.

[6] R. Usón, J. Forniés, M. Tomás, B. Menjón, *Organometallics* **1985**, *4*, 1912.

[7] Leading reviews: a) S. H. Strauss, *J. Chem. Soc. Dalton Trans.* **2000**, 1; b) H. Willner, F. Aubke, *Angew. Chem.* **1997**, *109*, 2506; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2402; c) C. Wang, G. Hwang, S. C. Siu, F. Aubke, B. Bley, M. Bodenbinder, C. Bach, H. Willner, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 917; d) J. E. Ellis, W. Beck, *Angew. Chem.* **1995**, *107*, 2695; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2489; e) F. Aubke, *J. Fluorine Chem.* **1995**, *72*, 195; f) L. Weber, *Angew. Chem.* **1994**, *106*, 1131; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1077; g) F. Aubke, C. Wang, *Coord. Chem. Rev.* **1994**, *137*, 483.

[8] R. Usón, J. Forniés, P. Espinet, R. Navarro, F. Martínez, M. Tomás, *J. Chem. Soc. Chem. Commun.* **1977**, 789.

[9] a) R. Usón, J. Forniés, *Adv. Organomet. Chem.* **1988**, *28*, 219; b) E. Maslowsky, Jr., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, **1977**, pp. 437–442.

[10] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, Section I-11, pp. 60–63.

[11] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, Section 17-G-3, pp. 838–842.

[12] a) J. Forniés, A. Martín in *Metal Clusters in Chemistry, Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, Section 1.22, pp. 418–443; b) R. Usón, J. Forniés, *Inorg. Chim. Acta* **1992**, *198–200*, 165; c) R. Usón, J. Forniés, M. Tomás, *J. Organomet. Chem.* **1988**, *358*, 525.

[13] R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *219–221*, 157.

[14] a) W. A. Sheppard, *J. Am. Chem. Soc.* **1970**, *92*, 5419; b) C. A. Tolman, *J. Am. Chem. Soc.* **1970**, *92*, 2953.

[15] R. Usón, J. Forniés, M. Tomás, R. Fandos, *J. Organomet. Chem.* **1984**, *263*, 253.

[16] M. M. Brezinski, J. Schneider, L. J. Radonovich, K. J. Klabunde, *Inorg. Chem.* **1989**, *28*, 2414.

[17] a) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927; b) K. Seppelt, *Angew. Chem.* **1993**, *105*, 1074; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1025; c) M. Bochmann, *Angew. Chem.* **1992**, *104*, 1206; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1181; d) G. A. Lawrance, *Adv. Inorg. Chem.* **1989**, *34*, 145; e) W. Beck, K. Sünkel, *Chem. Rev.* **1988**, *88*, 1405; f) G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17; g) N. M. N. Gowda, S. B. Naikar, G. K. N. Reddy, *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 255.

[18] A. Arcas, P. Royo, *Inorg. Chim. Acta* **1978**, *30*, 205.

[19] a) R. Usón, J. Forniés, M. Tomás, B. Menjón, *Organometallics* **1986**, *5*, 1581. b) B. Menjón, Ph.D. Thesis, Zaragoza, **1985**.

[20] M. M. Brezinski, K. J. Klabunde, *Organometallics* **1983**, *2*, 1116.

[21] R. G. Gastinger, B. B. Anderson, K. J. Klabunde, *J. Am. Chem. Soc.* **1980**, *102*, 4959.

[22] Data (40) were retrieved from the Cambridge Structural Database (see ref. [23]).

[23] F. H. Allen, J. E. Davies, J. J. Galloy, D. Johnson, O. Kennard, C. F. Macrae, E. M. Mitcher, G. F. Mitchell, J. M. Smith, D. G. Watson, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

[24] H. Hoberg, G. Burkhart, C. Krüger, Y.-H. Tsay, *J. Organomet. Chem.* **1981**, *222*, 343.

[25] N. G. Connelly, O. M. Hicks, G. R. Lewis, A. G. Orpen, A. J. Wood, *J. Chem. Soc. Dalton Trans.* **2000**, 1637.

[26] Data (22) were retrieved from the Cambridge Structural Database (see ref. [23]).

[27] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335.

[28] Data (60) were retrieved from the Cambridge Structural Database (see ref. [23]).

[29] W.-F. Liaw, Y.-C. Horng, D.-S. Ou, C.-Y. Ching, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.* **1997**, *119*, 9299.

[30] The crystal structures of the related species $[N(PPh_3)_2][Ni(SePh)_{3-x}(SPh)_x(CO)]$ were also determined ($Ni{-}C = 180(2)$ ($x = 1$) and 173.7(5) ($x = 2$) pm). Some bond lengths, however, were poorly determined due to severe S/Se disorder in both cases. W.-F. Liaw, C.-H. Chen, C.-M. Lee, G.-H. Lee, S.-M. Peng, *J. Chem. Soc. Dalton Trans.* **2001**, 138.

[31] C. Saint-Joly, A. Mari, A. Gleizes, M. Dartiguenave, Y. Dartiguenave, J. Galy, *Inorg. Chem.* **1980**, *19*, 2403.

[32] C. G. Pierpont, R. Eisenberg, *Inorg. Chem.* **1972**, *11*, 828.

[33] T. J. Groshens, K. J. Klabunde, *J. Organomet. Chem.* **1983**, *259*, 337.

[34] P. S. Braterman, *Metal Carbonyl Spectra*, Academic Press, London, **1975**, Section 7.2, pp. 177–179.

[35] S. K. Janikowski, L. J. Radonovich, T. J. Groshens, K. J. Klabunde *Organometallics* **1985**, *4*, 396.

[36] a) S. W. Ragsdale, M. Kumar, *Chem. Rev.* **1996**, *96*, 2515; b) M. A. Halcrow, G. Christou, *Chem. Rev.* **1994**, *94*, 2421.

[37] S. A. Macgregor, Z. Lu, O. Eisenstein, R. H. Crabtree, *Inorg. Chem.* **1994**, *33*, 3616.

[38] J. J. Bishop, A. Davison, *Inorg. Chem.* **1971**, *10*, 832.

[39] A. Miedaner, C. J. Curtis, S. A. Wander, P. A. Goodson, D. L. DuBois, *Organometallics* **1996**, *15*, 5185.

[40] M. Wada, K. Oguro, *Inorg. Chem.* **1976**, *15*, 2346.

[41] a) T.-t. Jzang, C.-y. Lee, C.-s. Liu, *Organometallics* **1988**, *7*, 1265; b) C.-s. Liu, C.-w. Cheng, *J. Am. Chem. Soc.* **1975**, *97*, 6746; c) C.-w. Cheng, C.-s. Liu, *J. Chem. Soc. Chem. Commun.* **1974**, 1013.

[42] B. von Ahsen, R. Wartchow, H. Willner, V. Jonas, F. Aubke, *Inorg. Chem.* **2000**, *39*, 4424.

[43] D. B. Dell'Amico, F. Calderazzo, C. A. Veracini, N. Zandonà, *Inorg. Chem.* **1984**, *23*, 3030.

[44] D. Costa, G. Martra, M. Che, L. Manceron, M. Kermarec, *J. Am. Chem. Soc.* **2002**, *124*, 7210.

[45] M. R. Churchill, M. V. Veidis, *J. Chem. Soc. Dalton Trans.* **1972**, 670.

[46] Data (13) were retrieved from the Cambridge Structural Database (see ref. [23]).

[47] a) C. S. Shultz, J. M. DeSimone, M. Brookhart, *J. Am. Chem. Soc.* **2001**, *123*, 9172; b) C. S. Shultz, J. M. DeSimone, M. Brookhart, *Organometallics* **2001**, *20*, 16.

[48] R. Usón, A. Laguna in *Inorganic Syntheses, Vol. 21* (Ed.: J. P. Fackler, Jr.), Wiley, New York, **1982**, Section 15.B, p. 72.

[49] N. S. Gill, F. B. Taylor in *Inorganic Syntheses, Vol. 9* (Ed.: S. Y. Tyree, Jr.), McGraw-Hill, New York, **1967**, Section 36, pp. 136–142.

[50] R. Usón, A. Laguna, L. A. Abad, *J. Organomet. Chem.* **1983**, *246*, 341.

[51] G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Germany **1997**.

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