

CARBONYL COMPOUNDS OF COBALT(II) AND NICKEL(II). REVERSIBLE ARENE–CARBON MONOXIDE EXCHANGE AND SIMILARITIES TO ANALOGOUS η^6 -ARENE COMPLEXES

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(Received May 19th, 1983)

Summary

Displacement of η^6 -arene in $(C_6F_5)_2Co(\eta^6\text{-toluene})$, $(Cl_3Si)_2Ni(\eta^6\text{-toluene})$, and $(F_3Si)_2Ni(\eta^6\text{-toluene})$ by CO yielded very labile $(C_6F_5)_2Co(CO)_3$, $(Cl_3Si)_2Ni(CO)_3$, and $(F_3Si)_2Ni(CO)_3$, which are rare examples of isolated, characterized, simple carbonyl complexes of cobalt(II) and nickel(II). According to infrared $\nu(C=O)$ studies the cobalt(II) tricarbonyl and the nickel(II) tricarbonyl derivatives are trigonal bipyramidal with the CO ligands in the axial positions. These η^6 -arene substitutions with CO are reversible under mild conditions. However, the cobalt system slowly degrades to cobalt(I) while the nickel system degrades to nickel(0) carbonyl compounds.

Introduction

Simple carbonyl complexes of cobalt(II) and nickel(II) are quite rare [1,2]. Attempts to prepare them, for example from $CoCl_2$ and $NiCl_2$, have led to unstable species, and it has been tacitly assumed that these higher oxidation states of Co and Ni could not effectively support the necessary donation-backbonding synergism of the M–CO bond [2].

Matrix isolation experiments, where NiF_2 and $NiCl_2$ have been codeposited with CO have led to unstable X_2NiCO complexes that displayed, according to vibrational spectra, a virtual absence of $d \rightarrow \pi^*$ backbonding [3]. Donation to nickel(II) was significant, however, and $\nu(C=O)$ for X_2NiCO were 2200 cm^{-1} ($X = F$) and 2189 cm^{-1} ($X = Cl$), both higher than free CO at 2143 cm^{-1} .

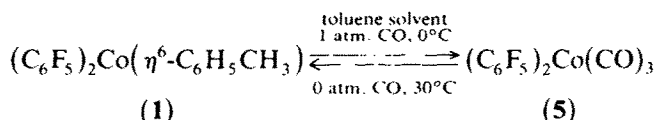
In recent years the first η^6 -arene complexes of cobalt(II) and nickel(II) complexes have been synthesized and structurally characterized [4]. The facile displacement of the η^6 -arene in $(C_6F_5)_2Co(\eta^6\text{-toluene})$ (1), $(C_6F_5)_2Ni(\eta^6\text{-toluene})$ (2), $(Cl_3Si)_2Ni(\eta^6\text{-toluene})$ (3), and $(F_3Si)_2Ni(\eta^6\text{-toluene})$ (4) has allowed the preparation of a series of new X_2ML_2 derivatives [5]. We report here that treatment of these η^6 -arene

complexes with CO leads to complete arene displacement, but reversibly so, with the formation of simple, isolable $X_2M(CO)_3$ derivatives.

Results

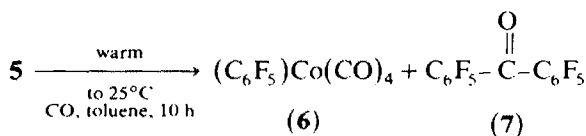
Treatment of **1** with carbon monoxide

Tricarbonyl bis(pentafluorophenyl)cobalt, $(C_6F_5)_2Co(CO)_3$ (**5**). Treatment of **1** in toluene at $0^\circ C$ with one atmosphere CO led to a slow color change from dark red-orange to green with the precipitation of light green crystals of **5**. Vacuum removal of the CO atmosphere followed by rapid warming to room temperature caused foaming and complete release of coordinated CO with the quantitative reformation of **1**. Cooling and readdition of CO caused the reformation of **5**; thus the reaction is completely reversible:



The isolation of **5** was carried out at $0^\circ C$ and its infrared spectrum recorded. A weighed sample was treated with excess toluene at room temperature and the CO released was trapped (Toepler pump), giving about 2.5 mol CO/mol **5** with some decomposition. Thus the stoichiometry of **5** is probably three CO/Co.

Compound **5** is extremely reactive and unstable. Allowing it to slowly warm under a CO atmosphere caused the following reaction [6] (over several hours):



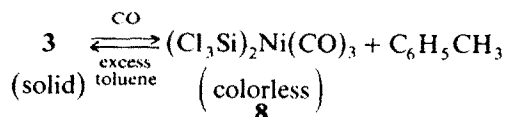
The infrared of **5** in toluene showed one strong $\nu(C=O)$ at 2108 cm^{-1} . No evidence for bridging CO ligands was found.

Treatment of **2** with carbon monoxide

Treatment of $(C_6F_5)_2Ni(\eta^6\text{-toluene})$ (**2**) in toluene with CO at $0^\circ C$ led to rapid and clean production of $Ni(CO)_4$ and $C_6F_5C_6F_5$ [4a]. This result reflects the more facile reductive elimination mode for the nickel(II) vs. the cobalt(II) system, which we have observed before [5].

Treatment of **3** with carbon monoxide

Tricarbonylbis(trichlorosilyl)nickel, $(Cl_3Si)_2Ni(CO)_3$ (**8**). Solid $(Cl_3Si)_2Ni(\eta^6\text{-toluene})$ (**3**) [7a,b] was treated with one atmosphere of CO, at room temperature. Over a 3 h period the red-orange solid turned to a colorless solid with the elimination of toluene. Compound **8** is a volatile solid that partially reverts to **3** in



toluene solvent (reversible). In arene solvents **8** is quite stable, but in alkanes it quickly decomposes to Ni(CO)_4 , $\text{Cl}_3\text{SiSiCl}_3$, and Ni metal. The $\nu(\text{C=O})$ for **8** is at 2079 cm^{-1} in Nujol, with no evidence of bridging CO ligands.

Treatment of 4 with carbon monoxide

Tricarbonylbis(trifluorosilyl)nickel, $(\text{F}_3\text{Si})_2\text{Ni(CO)}_3$ (**9**). Solid $(\text{F}_3\text{Si})_2\text{Ni}(\eta^6\text{-toluene})$ (**4**) [8] was treated with one atmosphere of CO causing the yellow color to change to colorless, solid **9**, plus toluene. In excess toluene **4** can be regenerated.

Discussion

Although these new compounds **5**, **8**, and **9** are reactive, possess labile CO ligands, and the $\nu(\text{C=O})$ values indicate little synergistic bonding, they are isolable. This is not the case for other similar metal(II) derivatives, for example CO adducts of NiF_2 and NiCl_2 . It is of interest to compare the observed $\nu(\text{C=O})$ values for this series of metal(II) derivatives as well as some metal(0) derivatives (Table 1). It appears that the CO lability can be predicted from the $\nu(\text{C=O})$ values, and further, that the ability of the decarbonylated metal center to form a π -arene complex can also be predicted as well as the π -arene lability. Thus, F_2Ni and Cl_2Ni centers very weakly interact with CO and not at all with arenes [9]. However, $(\text{C}_6\text{F}_5)_2\text{Co}$, $(\text{Cl}_3\text{Si})_2\text{Ni}$, and $(\text{F}_3\text{Si})_2\text{Ni}$ interact moderately well with CO forming isolable, labile complexes, and also form isolable π -arene complexes but which are labile. Lastly, the $(\text{diphos})\text{Fe}$, $(\text{CO})_3\text{W}$, $(\text{CO})_3\text{Mo}$, and $(\text{CO})_3\text{Cr}$ centers form strong bonds to additional CO ligands which are not labile, and have strong π -arene bonding with the resulting π -arene being non-labile. So to a rough approximation, carbonyl complexes with $\nu(\text{C=O})$ $2050\text{--}2100\text{ cm}^{-1}$ are likely candidates for yielding metal centers (after CO removal) forming labile but isolable π -arene complexes. Likewise, $\nu(\text{C=O})$ values of less than 2050 cm^{-1} would bode well for the metal center being capable of strongly binding arenes.

A further consideration is that **5**, **8**, and **9** will undergo CO displacement by

TABLE 1

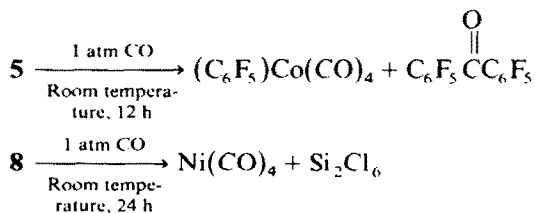
$\nu(\text{C=O})$ VALUES FOR SELECTED METAL CARBONYL COMPLEXES AND COMPARISONS WITH π -ARENE COMPLEXES

Compound ($x = 1$ or 2)	$\nu(\text{C=O})$ (cm^{-1})	Lability of CO	π -Arene Known? ^a	Lability of corresponding π -arene	Reference
$\text{F}_2\text{Ni(CO)}_x$	2200	high	does not form	—	3, 9
$\text{Cl}_2\text{Ni(CO)}_x$	2189	high	does not form	—	3, 9
$(\text{C}_6\text{F}_5)_2\text{Co(CO)}_3$	2110	highest	yes	highest	This work
$(\text{Cl}_3\text{Si})_2\text{Ni(CO)}_3$	2100	high	yes	high	This work
$(\text{F}_3\text{Si})_2\text{Ni(CO)}_3$	2100		yes	high	This work
$(\text{diphos})\text{Fe(CO)}_3$	1992, 1923 1901	low	yes	low	18a, b, 20
W(CO)_6	1987	low	yes	low	19, 20
Mo(CO)_6	1993	low	yes	low	19, 20
Cr(CO)_6	1990	low	yes	low	19, 20

^a Arene replaces three CO ligands for all compounds.

arenes. In fact the equilibria $M-(CO)_3 \rightleftharpoons M\text{-arene}$ is set up readily at moderate temperature and normal pressures. To our knowledge this is the first case of such equilibria being observed.

The reaction chemistry of **5** and **8** under excess CO indicates that reductive elimination from Ni of the σ -bound ligands is quite facile, which is also the case for the corresponding π -arene [4a,5,10]. In the cobalt case more complex reactions ensue. It is of particular interest that decafluorobenzophenone is formed (rather than decafluorobiphenyl) which would seem to require the hitherto unobserved CO insertion into a Co-C₆F₅ bond [11]:



The geometries and stoichiometries of **5**, **8**, and **9** should be discussed. As is commonly known Ni(CO)₄ is tetrahedral (Ni⁰) whereas X₂Ni(L)₂ derivatives (Ni²⁺) are generally square planar. The addition of a fifth ligand is less common and is very sterically dependent [12]. In the present study three CO ligands were added such that the compounds are isoelectronic with the starting arene complex. Since only one $\nu(C=O)$ band is observed, the structures must be trigonal bipyramidal [12,13]. Thus, these derivatives are sterically and electronically capable of accepting three CO ligands in equatorial positions.

The Co system is especially sensitive regarding geometry. Usually (C₆F₅)₂Co only adds two ligands and the resultant (C₆F₅)₂CoL₂ derivatives are tetrahedral [5]. However, strong π -acceptor phosphine ligands cause a shift to square planarity, eg. (C₆F₅)₂Co[P(C₂H₅)₃]₂ [14]. Molecular models indicate that addition of a third L group would be difficult for most ligands, although this is not the case for CO and P(CH₃)₃. So it is apparent that the geometry and stoichiometry of (C₆F₅)₂Co(L)_x are very sensitive to electronic and steric effects [15], and can be manipulated easily.

Experimental

Solvents were purified by refluxing over benzophenone ketyl. Infrared spectra were recorded on a Beckman IR-12; NMR on a Varian T-60 or XL-100; Mass spectra on a Finnigan GC-MS. Compounds **1**, **2** and **3** were synthesized as previously described [4,5,7a].

*Synthesis of (CO)₃Co(C₆F₅)₂ (**5**) and determination of CO content*

Compound **1** (1.0 g) was dissolved in 10 ml of dry, deoxygenated toluene. The resultant brown solution was cooled to 0°C and 1 atm CO added, which turned the solution dark green after 0.5 h. After 1.5 h total at 0°C bright green needle crystals formed on the walls of the reactor tube. The liquid was decanted and the crystals dried under vacuum at 0°C (yield about 25% isolated). IR (KBr pellet, cm⁻¹) 2130vs, 1625w, 1610w, 1530s, 1500vs, 1486vs, 1369w, 1350m, 1268w, 1182w, 1070s, 1050s, 1015m, 960vs, 775s, 530s, 498w, 455w, 445w, 382w, 356w, in the $\nu(C=O)$

region in Nujol 2120, in CCl_4 2110, in toluene 2108, and in C_6F_6 2110. Upon prolonged IR analysis, peaks due to the slowly growing impurity $\text{C}_6\text{F}_5\text{Co}(\text{CO})_4$ (2040vs, 2060s, 2122w) [16] appeared along with a 2143 cm^{-1} band for free CO. Compound **1** could be regenerated quantitatively from **5** by rapidly warming **1** to 30°C in toluene under vacuum. During this process the solution turned from green to red-brown, and $2.4\text{ mol CO}/1.0\text{ mol } \mathbf{1}$ generated was released, as determined by collecting the released CO by Toepler pump and doing a PV measurement. Compound **5** is not very stable and will decompose slowly at room temperature to a brown oil.

*Synthesis of $(\text{CO})_3\text{Ni}(\text{SiCl}_3)_2$ (**8**) and determination of CO content*

Finely divided $(\eta^6\text{-benzene})\text{Ni}(\text{SiCl}_3)_2$ (**10**) was produced by freeze drying from benzene (see later description for the preparation of this compound from the toluene derivative **3**). The benzene derivative was used because it could be obtained in a more finely divided form by the freeze drying method. Although **10** worked better, **3** could also be used to prepare **8**.

Compound **10** (5.6 g, 13.8 mmol) was placed in a 200 ml flask as a powder, and 1 atm of CO inletted. The heterogeneous mixture was allowed to stand for 3 h while the color of the solid changed from yellow-orange to colorless with the generation of some liquid. The liquid (benzene) was carefully removed under vacuum leaving colorless crystals of **8** (4.3 g, 76%), which is indefinitely stable at 0°C but will slowly degrade at room temperature to a mixture of Ni metal, $\text{Ni}(\text{CO})_4$ and $\text{Cl}_3\text{SiSiCl}_3$. IR (Nujol mull, cm^{-1}): 2089vs, 608w, 577s, 475s, 397w, in the $\nu(\text{C}=\text{O})$ region in Nujol 2089, in C_6F_6 2100 (upon prolonged IR analysis a peak at 2048 cm^{-1} for $\text{Ni}(\text{CO})_4$ grew in). Mass spectrum (chemical ionization using methane) $(\text{CO})_2\text{-Ni}(\text{SiCl}_3)(\text{SiCl}_2)^+$ and smaller $(\text{CO})_3\text{Ni}(\text{SiCl}_3)(\text{SiCl}_2)^+$ were obtained with the expected $\text{Cl}_5 + \text{Ni}$ isotope pattern (low resolution).

Compound **3** could be generated from **8** by heating to 80°C in excess toluene under vacuum. The solution changed from colorless to red-brown and $2.4\text{ mol}/1\text{ mol } \mathbf{3}$ generated was collected by a Toepler pump.

*Synthesis of $(\text{CO})_3\text{Ni}(\text{SiF}_3)_2$ (**9**)*

A few mg of powdered **4** (see later for preparation) was treated with 1 atm of CO for 0.5 h. The released toluene was carefully removed under vacuum leaving white $(\text{CO})_3\text{Ni}(\text{SiF}_3)_2$ (**9**), which is a sublimeable solid. IR in C_6F_6 $\nu(\text{C}=\text{O})$ 2100 cm^{-1} ; mass spectrum (chemical ionization using methane) $(\text{CO})_2\text{Ni}(\text{SiF}_3)(\text{SiF}_2)^+$ and smaller $(\text{CO})_3\text{Ni}(\text{SiF}_3)(\text{SiF}_2)^+$ were obtained with the expected Ni isotope pattern (low resolution).

*Synthesis of $(\eta^6\text{-C}_6\text{H}_6)\text{Ni}(\text{SiCl}_3)_2$ (**10**)*

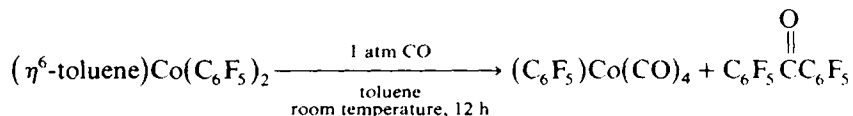
This benzene complex was prepared by exhaustive exchange of toluene from **3**. Thus, about 1 g of **3** was dissolved in 10 ml benzene and the volatiles removed under vacuum. This procedure was repeated yielding red-brown $(\eta^6\text{-C}_6\text{H}_6)\text{Ni}(\text{SiCl}_3)_2$ quantitatively; m.p. 133°C decomp. IR: 3085m, 1584vw, 1530vw, 1462s, 1450s, 1415w, 1380m, 1348vw, 1162w, 1090v broad, 1030w, 1013w, 993w, 988w, 928m, 790m, 777s, 675vw, 550vvs, 485vvs, 347m, 322s, 275w, 264w, 252s; NMR(δ) CDCl_3 : 7.0 (s).

Synthesis of $(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Ni}(\text{SiF}_3)_2$ **4**

A metal vapor reaction similar to those previously described [7a,17] was carried out. Nickel (1.6 g, 27.3 mg-atom), toluene (10 g, 109 mmol), and F_3SiSiF_3 (100 mmol) were codeposited at -196°C over a 2 h period. The resultant red-brown matrix was allowed to warm and melt. Excess toluene and F_3SiSiF_3 were removed under vacuum followed by washing the dry black powder three times with 20 ml toluene, then filtering the light yellow solution under nitrogen. The solvent was removed leaving about 50 mg of light yellow solid (m.p. 95°C slowly sublimates at 70°C in vacuo). IR (Nujol mull): 3115w, 1561m, 1525w, 1310w, 1257w, 900sh, 875vs, 833vs, 784vs, 728sh, 670w, 476s, 450s, 334s, 320s; NMR(δ) CDCl_3 : 2.5(s,3H) 6.8(s,5H); Mass spectrum chemical ionization using methane: parent peak $(\text{tol})\text{Ni}(\text{SiF}_3)_2^+$ 6%; $(\text{tol})\text{Ni}(\text{SiF}_3)(\text{SiF}_2)^+$ 100%; $(\text{tol})\text{Ni}(\text{SiF}_3)^+$ 11%. Analysis Found C, 26.68, H, 2.90, F, 36.71. $\text{C}_7\text{H}_8\text{F}_6\text{NiSi}_2$ calcd.: C, 26.18, H, 2.51, F, 35.51%.

Complete reaction of $(\text{toluene})\text{Co}(\text{C}_6\text{F}_5)_2$ (**1**) with CO (**5** as an intermediate)

If a toluene solution of $(\eta^6\text{-toluene})\text{Co}(\text{C}_6\text{F}_5)_2$ was allowed to stand for 12 h at room temperature under 1 atm CO, the color changed from brown to green after about 0.5 h. This green color faded slowly until after about 5 h the solution was light yellow and CO uptake stopped. Removal of excess toluene left a volatile light yellow compound identified by IR and MS as the known $(\text{C}_6\text{F}_5)\text{Co}(\text{CO})_4$ [16]. GC analysis of the recovered volatiles showed no $\text{C}_6\text{F}_6\text{H}$. When the $(\text{C}_6\text{F}_5)\text{Co}(\text{CO})_4$ was sublimed there was also a white solid that was identified by MS and IR as $(\text{C}_6\text{F}_5)_2\text{CO}$ [6].



Complete reaction of $(\text{toluene})\text{Ni}(\text{SiCl}_3)_2$ (**3**) with CO (**8** as an intermediate)

Solid **3** (0.512 g, 1.2 mmol) was dissolved in 2 ml benzene and freeze-thaw degassed after which 1 atm CO was added to the bulb and the solution stirred for 24 h at room temperature. The solution turned from red to colorless over a 4 h period. The final mixture was injected on a 10 ft. 25% SE30 Chromosorb Column at 135°C showing 30% Si_2Cl_6 (GC/MS) using toluene as a standard. IR showed the presence of $\text{Ni}(\text{CO})_4$ 2040 cm^{-1} .

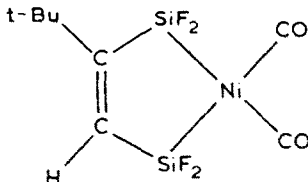
Attempted synthesis of $(\text{CO})_3\text{Ni}(\text{C}_6\text{F}_5)_2$

These experiments were carried out to see if by adding a limiting amount of CO to **1**, the dicarbonyl or tricarbonyl compound could be obtained, rather than $\text{C}_6\text{F}_5\text{C}_6\text{F}_5$ and $\text{Ni}(\text{CO})_4$ [4a]. In a 20 ml tube containing 0.1 g (0.2 mmol) of **1**, 380 mm (0.4 mmol) of CO was added and allowed to stand overnight. An IR study of the products in C_6F_6 showed $\text{Ni}(\text{CO})_4$ at 2040 cm^{-1} as the only carbonyl compound. The reaction was repeated by first dissolving the toluene compound in 2 ml of benzene to try and speed up the CO uptake. Again, IR analysis showed only $\text{Ni}(\text{CO})_4$. A white solid was also generated and was identified as $\text{C}_6\text{F}_5\text{C}_6\text{F}_5$. Thus, even with limited amounts of CO, **1** only yielded the products observed when excess CO was present [4a].

Acknowledgements

The generous support of the National Science Foundation is acknowledged with gratitude. We thank M. Brezinski for experimental assistance.

References and notes

- 1 A few η^3 -allyl- and η^5 -cyclopentadienyl-nickel carbonyls are known, i.e. $(\eta^6\text{-C}_3\text{H}_5)_2\text{Ni(CO)Cl}$, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni(CO)}]_2$, and $(\eta^5\text{-C}_5\text{H}_5)\text{Ni(CO)I}$, as well as $\text{CoX}_2(\text{CO})(\text{PR}_3)_2$ complexes; R.D.W. Kemmitt and D.R. Russell, in G. Wilkinson, F.G.A. Stone, and E.W. Abel, (Eds.), *Comp. Organomet. Chem.*, 5 (34) 1, 40, 1982.
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Two $\nu(\text{C}=\text{O})$ at 2090 and 2040 cm^{-1} . C.S. Liu and C.W. Cheng, *J. Am. Chem. Soc.*, 97 (1975) 6746; (b) P. Royo and A. Vazquez, *J. Organomet. Chem.*, 205 (1981) 223 have prepared some interesting pentacoordinate $(\text{C}_6\text{F}_5)_2\text{Co(L)}_2\text{CO}$ derivatives.
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- 4 (a) R.G. Gastinger, B.B. Anderson, and K.J. Klabunde, *J. Am. Chem. Soc.*, 102 (1980) 4959; (b) K.J. Klabunde, B.B. Anderson, M. Bader, and L.J. Radonovich, *ibid.*, 100 (1978) 1313; (c) B.B. Anderson, C. Behrens, L.J. Radonovich, and K.J. Klabunde, *ibid.*, (1976) 5390.
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- 6 During this reaction green 5 changed to yellow 6. Both 6 and 7 were isolated pure by sublimation and identified by MS and IR.
- 7 (a) T.J. Groshens and K.J. Klabunde, *Organometallics*, 1 (1982) 564; (b) The benzene derivative could also be used and in fact gave higher yields, see Experimental section.
- 8 A new compound prepared by oxidative addition of F_3SiSiF_3 to Ni atoms in the presence of toluene (see ref. 7 for a general description using $\text{Cl}_3\text{SiSiCl}_3$ analogously, also see Experimental section).
- 9 According to unpublished work of Y. Tanaka from this laboratory showing that codeposited NiF_2 and NiCl_2 molecules (from vapor state) do not interact with benzene in a 10 K argon matrix. Interestingly, $\text{F}_2\text{Ni-C}_2\text{H}_4$ does form a complex showing $\nu(\text{C}=\text{C})$ at 1556 cm^{-1} with a pale purple color.
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