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# *o*-Isocyanobenzyl Complexes of Transition Metals as Novel Organometallic Isocyanide Ligands, $(\eta^5\text{-}C_5H_5)M(CO)_3(o\text{-}CH_2C_6H_4NC)$ (M = Mo, W) and $Mn(CO)_5(o\text{-}CH_2C_6H_4NC)$. Synthesis and Reactivity toward Palladium(II) and Platinum(II) Substrates

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Organometallic isocyanides of the general formula *o*-$([M]CH_2)C_6H_4NC$ ([M] = $CpMo(CO)_3$, $CpW(CO)_3$ (Cp = $\eta^5$-$C_5H_5$), $Mn(CO)_5$) were prepared by reaction of *o*-$(ICH_2)C_6H_4NC$ with the corresponding metal carbonyl anion. They are slightly foul-smelling solids that are stable for months under an inert atmosphere in the cold and in the dark. All the analytical and spectroscopic data confirm the uncoordination of the isocyanide function. Its coordinating capability has been tested in reactions involving Pd(II) and Pt(II) substrates and leading to the formation of heterobinuclear complexes of the type *cis*-$M'Cl_2(PR_3)(CN\frown CH_2[M])$ (M′ = Pd, Pt; $PR_3$ = $PPh_3$; [M] = $CpMo(CO)_3$, $CpW(CO)_3$, $Mn(CO)_5$; M′ = Pt; $PR_3$ = $PMePh_2$, [M] = $CpW(CO)_3$) and heterotrinuclear species of the type *cis*-$M'Cl_2(CN\frown CH_2[M])_2$ (M′ = Pd, Pt; [M] = $CpW(CO)_3$). Insertion reaction of $[W]CH_2\frown NC$ into the Pt–H bond of *trans*-$PtHCl(PPh_3)_2$ gives the formimidoyl derivative *trans*-$PtCl(PPh_3)_2(CHN\frown CH_2[W])$. Although the isocyanide groups in the $[M]CH_2\frown NC$ complexes are sterically incapable of chelation, they can potentially undergo insertion into the adjacent M–C σ-bond or intermolecular carbonyl substitution. However the thermal behavior of the $[Mo]CH_2\frown NC$ and $[W]CH_2\frown NC$ ligands shows extensive decomposition without any evidence for the occurrence of such reactions. Heating of $[Mn]CH_2\frown NC$ leads instead to the dimer $[Mn(CO)_4(o\text{-}CH_2C_6H_4NC)]_2$ in which the isocyanobenzyl moiety bridges two $Mn(CO)_4$ groups and whose structure was assigned by analogy of its IR spectrum with that of the *o*-cyanobenzyl analogue $[Mn(CO)_4(o\text{-}CH_2C_6H_4CN)]_2$.

## Introduction

The transition-metal coordination chemistry of isocyanide ligands containing functional substituents attracts considerable interest because of the reactivity and catalytic applications of the resulting complexes.[1-10] It appears also that the nature of the function may dictate the overall properties of the metal–ligand system.

We have recently shown[11] that the chemical behavior of functionalized isocyanides of the type *o*-$(XCH_2)C_6H_4NC$ (X = Cl, I) can be depicted as shown in A–C. The ligands

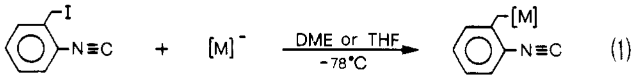
$[M]-C\equiv N\frown CH_2X$ A

$[M]-C\equiv N\frown CH_2-[M']$ B

$[M]-CH_2\frown N\equiv C$ C

can act as monodentate agents to give "open-chain" mononuclear derivatives by complexation of the isocyanide function (species of type A) or as bifunctional entities to give homo- and heterobinuclear complexes by involvement of both the isocyanide and alkyl halide ($CH_2X$) functions (species of type B). However, no complexes were isolated so far containing the metal σ-bonded alkyl function bearing the uncoordinated isocyanide moiety (species of type C).

We report in this paper the synthesis of novel, stable organometallic isocyanide ligands containing a transition-metal atom, which have been prepared by reaction of *o*-(iodomethyl)phenyl isocyanide[11] with the corresponding metal carbonyl anion according to eq 1.



$[M] = (\eta^5C_5H_5)Mo(CO)_3$ , $[Mo]CH_2\frown NC$

$[M] = (\eta^5C_5H_5)W(CO)_3$ , $[W]CH_2\frown NC$

$[M] = Mn(CO)_5$ , $[Mn]CH_2\frown NC$

We also describe the reactivity of these ligands, which is of interest for the following reasons. First, there appears to be no precedent for the isolation of such a class of compounds containing an uncoordinated isocyanide group within an organotransition-metal fragment. However, such complexes have been postulated as intermediates in the $Cu_2O$-catalyzed intramolecular cyclization of several isocyanides of the type *o*-$(XCH_2)C_6H_4NC$ (X = CN, COR, CONHR, $CO_2R$) to produce indole derivatives, which involves as the key step the formation of organocopper(I) isocyanide complexes.[3,5,6] In our case, a similar process would lead to a cyclic iminoacyl derivative.

Secondly, molecular models indicate that the isocyanide groups in these complexes are sterically incapable of chelation since the two metal-coordinated donors should form a 90° angle to each other as in square-planar and

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Table I. Analytical Data

| compd | C calcd | C found | H calcd | H found | N calcd | N found |
|---|---|---|---|---|---|---|
| ($\eta^5$-$C_5H_5$)Mo(CO)$_3$(*o*-$CH_2C_6H_4NC$) ([Mo]$CH_2\frown NC$) | 53.20 | 53.46 | 3.06 | 3.14 | 3.87 | 3.80 |
| ($\eta^5$-$C_5H_5$)W(CO)$_3$(*o*-$CH_2C_6H_4NC$) ([W]$CH_2\frown NC$) | 42.79 | 42.91 | 2.47 | 2.35 | 3.12 | 3.07 |
| Mn(CO)$_5$(*o*-$CH_2C_6H_4NC$) ([Mn]$CH_2\frown NC$) | 50.18 | 49.70 | 1.94 | 2.05 | 4.50 | 3.97 |
| *cis*-PdCl$_2$(PPh$_3$)($CN\frown CH_2$[Mo]) (**1**) | 50.99 | 51.37 | 3.27 | 3.37 | 1.75 | 1.58 |
| *cis*-PdCl$_2$(PPh$_3$)($CN\frown CH_2$[W]) (**2**) | 45.95 | 46.06 | 2.95 | 2.92 | 1.58 | 1.53 |
| *cis*-PdCl$_2$(PPh$_3$)($CN\frown CH_2$[Mn]) (**3**) | 49.60 | 49.24 | 2.82 | 3.00 | 1.87 | 1.44 |
| *cis*-PtCl$_2$(PPh$_3$)($CN\frown CH_2$[Mo]) (**4**) | 45.91 | 45.46 | 2.95 | 2.90 | 1.58 | 2.02 |
| *cis*-PtCl$_2$(PPh$_3$)($CN\frown CH_2$[W]) (**5**) | 41.78 | 41.47 | 2.68 | 2.67 | 1.43 | 1.49 |
| *cis*-PtCl$_2$(PPh$_3$)($CN\frown CH_2$[Mn]) (**6**) | 44.35 | 44.17 | 2.52 | 2.64 | 1.67 | 1.94 |
| *cis*-PtCl$_2$(PMePh$_2$)($CN\frown CH_2$[W]) (**7**) | 38.05 | 38.07 | 2.64 | 2.60 | 1.53 | 1.48 |
| *cis*-PdCl$_2$($CN\frown CH_2$[W])$_2$ (**8**) | 35.73 | 36.24 | 2.06 | 2.14 | 2.60 | 2.61 |
| *cis*-PtCl$_2$($CN\frown CH_2$[W])$_2$ (**9**) | 33.01 | 33.54 | 1.91 | 1.90 | 2.41 | 2.32 |
| *trans*-PtCl(PPh$_3$)$_2$($CHN\frown CH_2$[W]) (**10**) | 51.81 | 51.38 | 3.51 | 3.47 | 1.16 | 1.17 |

octahedral complexes. It is therefore expected that the coordination capability of the isocyanide function would lead to the formation of dimers rather than monomers. They may be either homonuclear, deriving for instance from intermolecular carbonyl substitution (formation of oligomers cannot be a priori ruled out), or heteropolynuclear, according to an appropriate choice of the metal substrates. In the latter case there would be the opportunity to obtain new complexes containing metal centers with different electronic configuration and chemical environment in close proximity.

## Experimental Section

**General Procedures and Materials.** All reactions were carried out under an inert atmosphere. Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), diethyl ether, and benzene were distilled under nitrogen from sodium/benzophenone before use. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification.

IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. $^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data were obtained on a Varian FT-80A spectrometer. $^{13}C$ NMR solutions contained Cr(acac)$_3$ (~0.02 M, acac = acetylacetonate) to reduce data collection time. In all the NMR spectra negative chemical shifts are upfield from the reference used. Mass spectra were recorded on a VG ZAB2F spectrometer. Melting points were taken on a hot plate apparatus and are uncorrected. Elemental analyses were performed at the Institute of Analytical Chemistry of the University of Padua. The *o*-(iodomethyl)phenyl isocyanide ligand was prepared as recently described.[11] The complexes [CpM(CO)$_3$]$^-$ [12] (M = Mo, W), [PdCl$_2$(PPh$_3$)]$_2$,[11] [PtCl$_2$(PR$_3$)]$_2$[13] (PR$_3$ = PPh$_3$, PMePh$_2$), PdCl$_2$(MeCN)$_2$,[11] (COD)PtCl$_2$[14] (COD = 1,5-cyclooctadiene), and *trans*-PtHCl(PPh$_3$)$_2$[15] were prepared according to the cited procedures.

**Preparation of Ligands. (*o*-Isocyanobenzyl)cyclopentadienyltricarbonylmolybdenum, ($\eta^5$-$C_5H_5$)Mo(CO)$_3$(*o*-$CH_2C_6H_4NC$) ([Mo]$CH_2\frown NC$).** To a solution of CpMo(CO)$_3^-$ (ca. 10.5 mmol) in DME (60 mL), previously cooled to −78 °C in a dry ice–acetone bath, was added in one portion solid *o*-(iodomethyl)phenyl isocyanide (2.43 g, 10.0 mmol). It was then stirred at the low temperature for 30 min and then slowly warmed to −20 °C in 3 h. It was taken to dryness at this low temperature and the crude reaction mixture product taken up with toluene (30 mL) and quickly filtered. The filtrate was passed through a short Florisil column (2 × 10 cm) and concentrated to small volume (5 mL). On addition of pentane (50 mL) and cooling to −78 °C a yellow precipitate of the product was obtained, which was washed with cold pentane and dried under vacuum: yield, 1.74 g or 48.2% (based on the isocyanide); Mp >90 °C (with darkening); analytical and spectroscopic data for this and the other ligands are listed in Tables I–III; $^{13}C\{^1H\}$ NMR (CDCl$_3$, $\delta$, chemical shifts reported from Me$_4$Si by taking the chemical shift of chloroform-*d* as +77.0 ppm) 238.5 (CO trans to CH$_2$), 227.5 (CO cis to CH$_2$), 164.5 (NC), 148.9, 128.6, 127.7, 125.8, 123.3 (C$_6$H$_4$), 93.0 (Cp), −3.2 (CH$_2$); mass spectrum showed M$^+$ at *m/e* 383 (for $^{98}$Mo) and peaks for [M − *n*(CO)]$^+$ (*n* = 2, 3).

**(*o*-Isocyanobenzyl)cyclopentadienyltricarbonyltungsten, ($\eta^5$-$C_5H_5$)W(CO)$_3$(*o*-$CH_2C_6H_4NC$) ([W]$CH_2\frown NC$).** To a stirred solution of CpW(CO)$_3^-$ (ca. 10.5 mmol) in DME (80 mL) at −78 °C was added in one portion solid *o*-(iodomethyl)phenyl isocyanide (2.43 g, 10.0 mmol). The resulting reaction mixture was slowly warmed to 0 °C in ca. 3 h. It was then evaporated to dryness under reduced pressure to yield a yellow solid that was dissolved in the minimum amount of benzene, filtered, and chromatographed on a Florisil column (3 × 40 cm) with Et$_2$O as eluant. The yellow band formed was collected and the ethereal solution taken to dryness to give a yellow solid that was found to contain in many repetitive preparations traces of unreacted W(CO)$_6$. The hexacarbonyl could be easily removed by sublimation at 50 °C and 1 × 10$^{-2}$ torr onto a dry ice cold probe: total yield, 2.9 g or 65% (based on the isocyanide); mp >100 °C (with darkening); $^{13}C\{^1H\}$ NMR (CDCl$_3$, $\delta$) 227.2 (CO trans to CH$_2$), 217.8 (CO cis to CH$_2$), 165.2 (NC), 149.5, 128.6, 127.7, 125.7, 123.4 (C$_6$H$_4$), 91.6 (Cp), −15.0 (CH$_2$); mass spectrum showed M$^+$ at *m/e* 448 (for $^{183}$W) and peaks for [M − *n*(CO)]$^+$ (*n* = 2, 3).

**(*o*-Isocyanobenzyl)pentacarbonylmanganese, Mn(CO)$_5$(*o*-$CH_2C_6H_4NC$) ([Mn]$CH_2\frown NC$).** Na/Hg prepared from Na (0.347 g) and Hg (6 mL) was treated dropwise in ca. 20 min with fast mechanical stirring with a solution of Mn$_2$(CO)$_{10}$ (2.25 g, 5.78 mmol) in THF (50 mL). The reaction mixture was left stirring at room temperature for 3 h. The solution was then filtered and cooled to −78 °C. Solid *o*-(iodomethyl)phenyl isocyanide (2.52 g, 10.4 mmol) was added in one portion and the reaction mixture allowed to reach −20 °C in ca. 3 h. This was subsequently taken to dryness at −20 °C, taken up with toluene (30 mL), and filtered. The deep orange solution was quickly passed through a short column (2 × 10 cm) of Florisil. Once collected, it was reduced to small volume (5 mL), pentane added (50 mL), and the solution stored at −78 °C for 3 days. The yellow precipitate formed was filtered, washed with cold pentane (2 × 10 mL), and dried under vacuum: yield, 2.25 g or 69.5%; mp >65 °C (with darkening); $^{13}C\{^1H\}$ NMR (CDCl$_3$, $\delta$) 210.8 (CO, broad signal), 167.1 (NC), 148.8, 129.0, 126.9, 126.8, 123.6 (C$_6$H$_4$), 4.2 (CH$_2$); mass spectrum showed M$^+$ at *m/e* 312 and peaks for [M − *n*(CO)]$^+$ (*n* = 1–5).

**Preparation of Complexes. *cis*-M′Cl$_2$(PR$_3$)($CN\frown CH_2$[M]) (1–7).** The complexes **1–6** (see also Tables I–III) where M′ = Pd and Pt, PR$_3$ = PPh$_3$, and [M] = CpMo(CO)$_3$, CpW(CO)$_3$, and Mn(CO)$_5$ and complex **7** where M′ = Pt, PR$_3$ = PMePh$_2$, and [M] = CpW(CO)$_3$ were prepared by the same standard procedure that is described below for complex **5**. To a suspension of [PtCl$_2$-

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**Table II. IR Spectral Data for the Ligands and Their Pd(II) and Pt(II) Complexes**

| compd | solv | $\nu$(N≡C), cm$^{-1}$ | $\nu$(C≡O), cm$^{-1}$ | other,$^a$ cm$^{-1}$ |
|---|---|---|---|---|
| $(\eta^5\text{-}C_5H_5)Mo(CO)_3(o\text{-}CH_2C_6H_4NC)$ ($[Mo]CH_2\frown NC$) | hexane | 2117 w | 2026 vs, 1951 vs, 1939 vs | |
| | $CH_2Cl_2$ | 2122 w | 2022 s, 1932 vs, br | |
| $(\eta^5\text{-}C_5H_5)W(CO)_3(o\text{-}CH_2C_6H_4NC)$ ($[W]CH_2\frown NC$) | hexane | 2118 w | 2022 vs, 1941 vs, 1933 vs | |
| | $CH_2Cl_2$ | 2123 w | 2018 vs, 1921 vs, br | |
| $Mn(CO)_5(o\text{-}CH_2C_6H_4NC)$ ($[Mn]CH_2\frown NC$) | hexane | 2113 w | 2113 m, 2053 m, 2017 vs, 1997 vs | |
| | $CH_2Cl_2$ | 2116 w | 2112 m, 2018 vs, 1995 s | |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[Mo])$ (**1**) | $CH_2Cl_2$ | 2209 m | 2019 s, 1924 s | $\nu$(PdCl) 338 m, 295 m |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[W])$ (**2**) | $CH_2Cl_2$ | 2212 m | 2022 s, 1915 s | $\nu$(PdCl) 342 m, 302 m |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[Mn])$ (**3**) | $CH_2Cl_2$ | 2206 m | 2113 m, 2017 vs, 1996 s, sh | $\nu$(PdCl) 342 m, 296 m |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[Mo])$ (**4**) | $CH_2Cl_2$ | 2205 m | 2019 s, 1925 s | $\nu$(PtCl) 340 m, 306 m |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[W])$ (**5**) | $CH_2Cl_2$ | 2204 m | 2019 s, 1915 s | $\nu$(PtCl) 342 m, 307 m |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[Mn])$ (**6**) | $CH_2Cl_2$ | 2201 m | 2112 m, 2017 s, 1996 s, sh | $\nu$(PtCl) 342 m, 301 m |
| *cis*-$PtCl_2(PMePh_2)(CN\frown CH_2[W])$ (**7**) | $CH_2Cl_2$ | 2192 m | 2019 s, 1914 s | $\nu$(PtCl) 340 m, 299 m |
| *cis*-$PdCl_2(CN\frown CH_2[W])_2$ (**8**) | $CH_2Cl_2$ | 2225 sh, 2210 w | 2020 s, 1914 vs, br | $\nu$(PdCl) 340 m, 319 m |
| *cis*-$PtCl_2(CN\frown CH_2[W])_2$ (**9**) | $CH_2Cl_2$ | 2230 w, 2205 m | 2021 s, 1912 vs, br | $\nu$(PtCl) 350 m, 329 m |
| *trans*-$PtCl(PPh_3)_2(CHN\frown CH_2[W])$ (**10**) | $CH_2Cl_2$ | | 2006 s, 1913 vs, br | $\nu$(PtCl) 273 w,<br>$\nu$(C=N) 1552 m |

[a] Nujol mull; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

**Table III. $^1H$ and $^{31}P\{^1H\}$ NMR Spectral Data[a]**

| | $^1H$ NMR | | $^{31}P\{^1H\}$ NMR | |
|---|---|---|---|---|
| compd | $\delta(CH_2)$ | $\delta(\eta^5\text{-}C_5H_5)$ | $\delta$(P) | $^1J$(P-Pt), Hz |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_3(o\text{-}CH_2C_6H_4NC)$ ($[Mo]CH_2\frown NC$) | 2.84 s | 5.42 s | | |
| $(\eta^5\text{-}C_5H_5)W(CO)_3(o\text{-}CH_2C_6H_4NC)$ ($[W]CH_2\frown NC$) | 2.90 s | 5.52 s | | |
| $Mn(CO)_5(o\text{-}CH_2C_6H_4NC)$ ($[Mn]CH_2\frown NC$) | 2.36 s | | | |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[Mo])$ (**1**) | 2.84 s | 5.58 s | 23.58 s | |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[W])$ (**2**) | 2.89 s | 5.69 s | 27.98 s | |
| *cis*-$PdCl_2(PPh_3)(CN\frown CH_2[Mn])$ (**3**) | 2.29 s | | 27.56 s | |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[Mo])$ (**4**) | 2.79 s | 5.55 s | 8.50 s | 3362 |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[W])$ (**5**) | 2.83 s | 5.65 s | 8.49 s | 3365 |
| *cis*-$PtCl_2(PPh_3)(CN\frown CH_2[Mn])$ (**6**) | 2.23 s | | 8.42 s | 3356 |
| *cis*-$PtCl_2(PMePh_2)(CN\frown CH_2[W])^b$ (**7**) | 2.82 s | 5.65 s | −2.53 s | 3258 |
| *cis*-$PdCl_2(CN\frown CH_2[W])_2$ (**8**) | 2.94 s | 5.65 s | | |
| *cis*-$PtCl_2(CN\frown CH_2[W])_2$ (**9**) | 2.94 s | 5.64 s | | |
| *trans*-$PtCl(PPh_3)_2(CHN\frown CH_2[W]^c$ (**10**) | 2.21 s | 5.59 s | 23.78 s | 2697 |

[a] Spectra recorded in $CD_2Cl_2$; proton chemical shifts reported from $Me_4Si$ by taking the chemical shift of dichloromethane-$d_2$ as +5.32 ppm; phosphorus chemical shifts referenced to external $H_3PO_4$ (85%); s = singlet, d = doublet. [b] PMe; $\delta$ 2.41 (d, $^2J$(H–P) = 11.8 Hz, $^3J$(H–Pt) = 35.0 Hz). [c] Methine CH: $\delta$ 8.70 (br signal).

$(PPh_3)]_2$ (1.04 g, 1.0 mmol) in $C_6H_6$ (30 mL) was added via a cannula a solution of $[W]CH_2\frown NC$ (0.99 g, 2.2 mmol) in $C_6H_6$ (30 mL) at room temperature. The yellow-orange solution obtained was stirred for 1 h. It was then concentrated to small volume and $Et_2O$ (40 mL) added. The yellow solid formed was filtered and recrystallized from $CH_2Cl_2/Et_2O$: yield, 1.55 g, 79.9%; mp 248–250 °C dec. The yields of the other complexes were in the 55–70% range, and the melting points are as follows: **1**, >200 °C (with darkening); **2**, 237–239 °C dec; **3**, 206–208 °C dec; **4**, >210 °C (with darkening); **6**, >220 °C (with darkening); **7**, 187–189 °C dec.

***cis*-$PdCl_2(CN\frown CH_2[W])_2$ (8).** A solution of $[W]CH_2\frown NC$ (0.66 g, 1.46 mmol) in $C_6H_6$ (30 mL) was added dropwise with stirring over a period of 10 min to a suspension of $PdCl_2(MeCN)_2$ (0.17 g, 0.66 mmol) in $C_6H_6$ (30 mL) at room temperature. The reaction mixture was stirred for an additional 30 min, and then the solution was reduced to small volume. $Et_2O$ (40 mL) was added to give a yellow solid which was filtered off and dried under vacuum: yield 0.52 g, 73.2%; mp 156–158 °C dec.

***cis*-$PtCl_2(CN\frown CH_2[W])_2$ (9).** This compound was prepared as reported for complex **8** starting from $(COD)PtCl_2$ (0.19 g, 0.5 mmol) and $[W]CH_2\frown NC$ (0.49 g, 1.1 mmol): yield 0.44 g, 76%; mp 178–180 °C dec.

***trans*-$PtCl(PPh_3)_2(CHN\frown CH_2[W])$ (10).** To a solution of *trans*-$PtHCl(PPh_3)_2$ (0.25 g, 0.33 mmol) in $C_6H_6$ (30 mL) was added via a cannula a benzene solution (10 mL) of $[W]CH_2\frown NC$ (0.164 g, 0.36 mmol). The reaction mixture was stirred at room temperature for 6 h. On concentration under reduced pressure to half of its volume a yellow solid precipitated. $Et_2O$ (15 mL) and pentane (15 mL) were added. The yellow solid was filtered off and recrystallized from $CH_2Cl_2$/MeOH: yield 0.12 g, 30%; mp 170–172 °C dec.

**Thermal Reaction of $[Mn]CH_2\frown NC$.** A solution of $[Mn]CH_2\frown NC$ (0.31 g, 1.0 mmol) in THF (30 mL) was refluxed under $N_2$ for 3 days. The deep brown reaction mixture was then evaporated to dryness under reduced pressure, taken up with benzene (10 mL), and filtered and the filtrate chromatographed on a Florisil column (3 × 30 cm). Eluting with *n*-hexane a pale yellow fraction was collected and shown to be $Mn_2(CO)_{10}$ by IR comparison with an authentic sample. Subsequent elution with hexane/dichloromethane (9/1 v/v) gave a second yellow band.

It was collected and taken to dryness to give an oily residue which could not be recrystallized. Its structure was assigned as the dimer $[Mn(CO)_4(o\text{-}CH_2C_6H_4NC)]_2$ by comparison of its IR spectrum with that of the cyanobenzyl complex $[Mn(CO)_4(o\text{-}CH_2C_6H_4CN)]_2$: IR (*n*-hexane) ν(NC) 2145 (m) $cm^{-1}$, ν(CO) 2079 (m), 2001 (vs), 1984 (m), 1964 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, δ, reference $Me_4Si$) 2.17 ($CH_2$).

## Results and Discussion

**Synthetic Aspects.** The basic route to the synthesis of the organometallic isocyanides, which will be referred to as $[M]CH_2\frown NC$ throughout, outlined in eq 1 (see Introduction) takes advantage of the well-known ability of organic halides to react with metal carbonyl anions to form M–C σ-bonds.[16] Examples of reactions of metal carbonyl anions with organic halides containing a functional group potentially capable of interacting with transition-metal systems have been reported in the past.[17]

Reaction 1 was found to give higher yields of products when the following were taken into account: (i) use of the more reactive *o*-(iodomethyl)phenyl isocyanide instead of the parent chloro compound; (ii) use of only a slight excess of the metal carbonyl anion; (iii) low-temperature (−78 °C) initial reaction conditions. In this way, the isocyanide ligands could be obtained in 48–70% yield. However, the analogous reaction using $CpFe(CO)_2^-$ did not produce the expected alkylated iron derivative but an unidentified brown material that, on the basis of IR evidence, did not contain the NC function. The failure to carry out this reaction can be attributed to the extremely high nucleophilicity[18] of $CpFe(CO)_2^-$ relative to the other monoanions employed that accounts, for instance, for its unique ability to displace fluoride from hexafluorobenzene.[19]

The isocyanide ligands prepared are yellow, crystalline, slightly foul-smelling solids. They are soluble in most organic solvents and are better stored under nitrogen in the cold and in the dark. As a general feature, the tungsten and manganese isocyanides appear to be the most stable in the series prepared, whereas dichloromethane or benzene solutions containing the molybdenum ligand undergo rapid darkening.

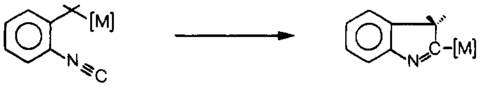
**Characterization.** The organometallic isocyanide ligands $[M]CH_2\frown NC$ have been characterized by a combination of elemental analysis (Table I) and IR (Table II), $^1H$ NMR (Table III), $^{13}C\{^1H\}$ NMR (see Experimental Section), and mass spectroscopy (Experimental Section). The uncoordinated isocyanide group in these compounds shows in the IR spectra (*n*-hexane solution) a weak to medium absorption in the 2112–2118 $cm^{-1}$ range, which is consistent with the values reported for free organic isocyanides of similar structure, $o\text{-}(XCH_2)C_6H_4NC$ (X = CN,[3] $CO_2R$,[3] COR,[5] CONHR,[6] Cl,[11] I[11]). If it were metal coordinated, the NC should have appeared at higher stretching frequencies as in related species $CpMo(CO)_2(CN\text{-}t\text{-}Bu)(COCH_2Ph)$[20] (ν(NC) 2137 (m) $cm^{-1}$ in $CH_2Cl_2$). On the other hand, the IR spectral pattern of terminal CO's clearly confirms the proposed configurations, similar to related benzyl carbonyl complexes of Mo,[11,21] W,[11,22] and Mn.[11,23,24]

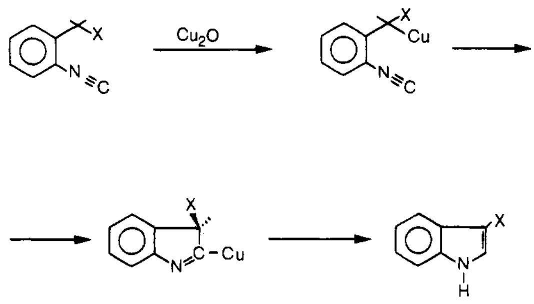
The $[M]CH_2\frown NC$ compounds show in the $^1H$ NMR spectra the methylene resonance as a sharp singlet in the δ 2.34–2.90 range, typical of σ-metal-bonded benzyl groups in complexes of analogous structure.[11,21-24] The unbonded NC moiety is unambiguously detected in the $^{13}C$ NMR spectra of solutions containing $Cr(acac)_3$ as a relaxation agent. The $[Mo]CH_2\frown NC$ and $[W]CH_2\frown NC$ ligands display the isocyanide carbon absorptions as broad signals due to $^{14}N$ coupling at ca. 165 ppm, with an upfield shift of about 3 ppm as compared to other free isocyanides of the type $o\text{-}(XCH_2)C_6H_4NC$ (X = Cl, I),[11] while the $^{13}C{\equiv}N$ of $[Mn]CH_2\frown NC$ appears at 167.5 ppm. All these values are normal for coordinated isocyanides.[25,26] By contrast, isocyanide coordination to W shifts the $^{13}C{\equiv}N$ resonance to ca. 156 ppm as in $W(CO)_5(CNC_6H_4\text{-}o\text{-}CH_2X)$[11] (X = Cl, I), whereas coordination to Mo in $Mo(CO)_4(DiNC)$[25] (DiNC = 1,2-bis(2-isocyanophenoxy)ethane) shifts it to 170 ppm. It should be noticed that the $^{13}C$ signal of a Mn-coordinated isocyanide is expected to be broadened by coupling with $^{14}N$ and also with Mn ($I = {}^5/_2$, 100% abundance) to such an extent as to be undetectable.

Also $^{13}CO$ and $^{13}CH_2$ resonances fall at the expected values for benzyl carbonyl complexes.[11,27,28]

Consistent with the above described formulations are the mass spectra of the $[M]CH_2\frown NC$ ligands for which a detailed examination of the fragmentation processes involved has not been attempted. Only the molecular ion, usually of low to medium intensity, and a few other major peaks are reported (see Experimental Section).

**Reactivity.** The chemistry of the organometallic isocyanides $[M]CH_2\frown NC$ explored focusing the attention on the possible roles of the NC function toward the reactive sites present in these molecules such as the M–C σ bond and the carbonyls. Although the NC group is uncoordinated in the $[M]CH_2\frown NC$ complexes, it was hoped that the direct insertion across the M–C σ-bond would lead, at least in principle, to the cyclic iminoacyl derivative: Related intramolecular insertions of isocyanides across Cu–C bonds, which are summarized in eq 2, have been reported[3,5,6] to occur in the $Cu_2O$-catalyzed synthesis of indole only with *o*-alkylphenyl isocyanides bearing a benzylic hydrogen activated by electron-withdrawing groups (eq 2).





(2)

X=CN, $CO_2R$, COR, CONHR

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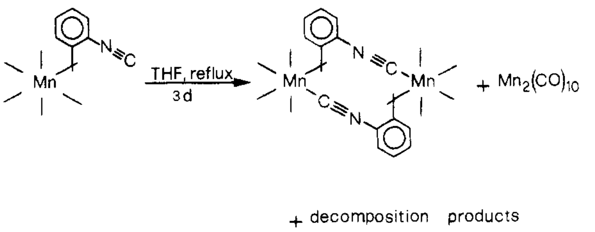
Insertion of isocyanide into the Mo–C $\sigma$-bond of CpMo(CO)$_3$(CH$_2$C$_6$H$_4$X-*p*) (X = Cl, H, OMe) has been reported[29] to occur easily in benzene at room temperature. A direct attack of the RNC ligand (R = $C_6H_{11}$) on the metal–carbon bond has been invoked, although a different reaction pathway has also been suggested.[30] Reaction of CpMo(CO)$_3$(CH$_2$Ph) with *t*-BuNC in refluxing benzene gave instead *fac*-(*t*-BuNC)$_3$Mo(CO)$_3$.[20] All other reported information on reactions of isocyanides with cyclopentadienylmetal carbonyl alkyls is limited to CpMo(CO)$_3$R (R = Me, CH$_2$Ph) type complexes giving the corresponding acyls CpMo(CO)$_2$(CNR)(COR).[20,29,31]

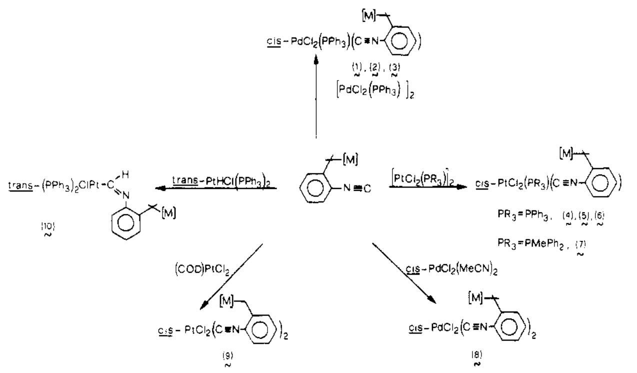
Actually, stirring the [Mo]$CH_2\frown NC$ compound in benzene at room temperature (2–3 days) or at reflux (1 d) did not give any evidence (IR and $^1$H NMR) for either the formation of iminoacyl or acyl derivatives or for species derived from carbonyl substitution. Instead, low soluble brown materials were recovered from the reaction mixtures. The [W]$CH_2\frown NC$ ligand showed a similar behavior, although it proved to be thermally more stable than the Mo analogue, thus reflecting the known thermal stability of W alkyls that can be attributed to a greater W–C bond strength compared to Mo.[32] The lack of reactivity shown by the [W]$CH_2\frown NC$ ligand parallels also the relatively great inertness found for the tungsten alkyls CpW(CO)$_3$R (R = Me, CH$_2$Ph).[33,34] On the contrary, the [Mn]$CH_2\frown NC$ compound gave some evidence for a different course of its thermal reaction that is outlined in eq 3. The structure of the dimer in which the *isocyanobenzyl* ligand bridges two Mn(CO)$_4$ moieties was assigned by analogy of its IR spectrum in the terminal CO's stretching region (solvent *n*-hexane, $\nu$(CO) = 2079, 2001, 1984, 1964 cm$^{-1}$) with the *cyanobenzyl* compound [Mn(CO)$_4$(*o*-CH$_2$C$_6$H$_4$CN)]$_2$[24] (solvent CCl$_4$, $\nu$(CO) = 2080, 2000, 1985, 1951 cm$^{-1}$). Coordination of the isocyanide ligand to Mn is supported by the value of its stretching frequency ($\nu$(NC) = 2145 cm$^{-1}$ in hexane). There appears to be no data in the literature for monoisocyanide alkyl carbonyl complexes of Mn. The MnBr(CO)$_4$(CNMe) compound has $\nu$(CN) at 2226 (m) cm$^{-1}$ in CHCl$_3$.[35] The presence of Mn$_2$(CO)$_{10}$ was confirmed by comparison of its infrared spectrum with that of an authentic sample. Its origin is not presently known but is probably due to a reductive coupling reaction that has been found to be operative in many transition-metal alkyls.[36]



(3)

The coordination ability of these organometallic isocyanide ligands has been exploited in reactions that are known to give stable metal isocyanide complexes with the corresponding organic isocyanides. These are summarized in Scheme I.

Scheme I



[a] For details about the [M] moiety see tables and Introduction.

The heterobinuclear complexes **1**–**7** and the heterotrinuclear species **8** and **9** have been characterized by conventional analytical and spectroscopic techniques (Tables I–III). All these compounds are stable for months in the solid state but slowly decompose in solution (especially those of Pd) at ambient temperature.

Diagnostic IR bands such as M–Cl and NC stretchings fall at the expected values for reported complexes of similar configuration.[11,37–39] Spectroscopic data indicate also that no interaction (i.e., ligand exchange) takes place between the metal carbonyl fragment and the M(II) (M = Pd, Pt) unit, each of them maintaining its original structure. The high $\Delta\nu = \nu(\mathrm{N{\equiv}C})_{\mathrm{coord}} - \nu(\mathrm{N{\equiv}C})_{\mathrm{free}}$[37] shift (ca. 80–90 cm$^{-1}$ for complexes **1**–**9**, Table II) suggests a high electrophilic character for the isocyanide carbon[37a] and therefore its potential ability to react with nucleophiles to form carbene complexes.[40]

The [W]$CH_2\frown NC$ ligand inserts into the Pt–H bond of *trans*-PtHCl(PPh$_3$)$_2$ to give the corresponding low soluble formimidoyl complex **10**, whose presence was confirmed by the characteristic[11,41] $\nu$(C=N) and $\nu$(Pt—Cl) IR bands at 1562 and 270 cm$^{-1}$, respectively. Compound **10** appears to exist as one single isomer as can be inferred by the presence in the $^1$H NMR spectrum of only one signal for the CH$_2$ and Cp resonances, while the methine proton was located at ca. $\delta$ 8.70 as an unresolved broad signal. Therefore the assignment of its geometry (syn or anti) could not be made as for related compounds.[41]

**Registry No.** 1, 91949-05-2; 2, 91949-06-3; 3, 91949-07-4; 4, 91949-08-5; 5, 91949-09-6; 6, 91949-10-9; 7, 91949-11-0; 8, 91949-12-1; 9, 91949-13-2; 10, 91993-45-2; ([Mo]$CH_2\frown NC$), 91949-14-3; ([W]$CH_2\frown NC$), 91949-15-4; ([Mn]$CH_2\frown NC$), 91949-16-5; [Mn(CO)$_4$(*o*-CH$_2$C$_6$H$_4$NC)]$_2$, 91949-17-6; [PdCl$_2$(PPh$_3$)]$_2$, 15134-30-2; [PtCl$_2$(PMePh$_2$)]$_2$, 16633-87-7; CpMo(CO)$_3^-$, 12126-18-0; CpW(CO)$_3^-$, 12126-17-9; Mn$_2$(CO)$_{10}$, 10170-69-1; [PtCl$_2$(PPh$_3$)]$_2$, 15349-80-1; PdCl$_2$(MeCN)$_2$, 14592-56-4; (COD)PtCl$_2$, 12080-32-9; *trans*-PtHCl(PPh$_3$)$_2$, 16841-99-9; *o*-(ICH$_2$)C$_6$H$_4$NC, 88644-60-4.

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