Contribution from the Centro di Chimica e Tecnologia Composti Metallorganici Elementi di Transizione CNR,
Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Padova, 35100 Padova, Italy

Functionalized Isocyanides as Ligands. Synthesis of 2-(Chloromethyl)- and 2-(Iodomethyl)phenyl Isocyanides and Their Transition-Metal Complexes

RINO A. MICHELIN,* GIACOMO FACCHIN, and PAOLO UGUAGLIATI

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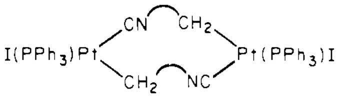
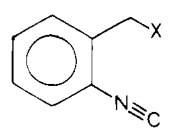
Isocyanides of the general structure 2-$(XCH_2)C_6H_4NC$ (X = Cl, 2-(chloromethyl)phenyl isocyanide ($CN\frown CH_2Cl$); X = I, 2-(iodomethyl)phenyl isocyanide ($CN\frown CH_2I$)) have been prepared through a four-step synthesis starting from 2-(chloromethyl)benzoyl chloride and proceeding through successive formation of the corresponding azide, isocyanate, and formamide. The iodo isocyanide was obtained from the parent chloride by halide exchange with NaI in acetone. Such ligands, which contain both isocyanide and alkyl halide (CH_2X) functions, can act as monofunctional or bifunctional ligands. Reactions involving the isocyanide function lead to mononuclear complexes of the type $M(CO)_5(CN\frown CH_2X)$ (M = Cr, W; X = Cl, I), *cis*-$MCl_2(PR_3)(CN\frown CH_2Cl)$ (M = Pd, Pt; PR_3 = PPh_3, $PMePh_2$, PMe_2Ph), and *cis*-$MCl_2(CN\frown CH_2Cl)_2$. Reaction of $CN\frown CH_2I$ with $[Pt(PMePh_2)Cl_2]_2$ yields a mixture of $PtClI(PMePh_2)(CN\frown CH_2Cl)$ (major product), $PtCl_2(PMePh_2)(CN\frown CH_2Cl)$, and $PtI_2(PMePh_2)(CN\frown CH_2I)$. Insertion reaction of $CN\frown CH_2Cl$ into the Pt–H bond in *trans*-$PtHCl(PPh_3)_2$ gives the formimidoyl complex *trans*-$PtCl(PPh_3)_2(CH{=}N\frown CH_2Cl)$. In some of these mononuclear isocyanide derivatives the dangling CH_2I function shows some typical reactions of halide displacement by aromatic amines or metal carbonyl anions, leading to new organometallic *o*-aminobenzyl isocyanide complexes of the type $M(CO)_5(CN\frown CH_2NH\text{-}p\text{-}C_6H_4Me)$ (M = Cr, W) and homo- and heterobinuclear derivatives of the types $M(CO)_5(CN\frown CH_2)M'Cp(CO)_3$ (M = Cr, M′ = Mo; M = W, M′ = Mo; M = M′ = W) and $W(CO)_5(CN\frown CH_2)Mn(CO)_5$. The CH_2I function in $M(CO)_5(CN\frown CH_2I)$ (M = Cr, W) also undergoes oxidative addition to Pd(0) and Pt(0) complexes, affording the binuclear complexes $M(CO)_5(CN\frown CH_2)$-*trans*-$M'I(PPh_3)_2$ (M = Cr, W, M′ = Pt; M = Cr, M′ = Pd). Oxidative addition of the uncoordinated $CN\frown CH_2I$ to $Pt(PPh_3)_2(C_2H_4)$ leads instead to the dimeric Pt(II) derivative



Introduction

Isocyanides with functional substituents such as alcohols,[1] esters,[2,3] ketones,[4,5] amides,[6] nitriles,[3] sulfones,[4,7] amines,[8] perhaloalkyls,[9] and α-acetylenic C atoms[10] have been reported in the recent past. Some of these owe their existence to stabilization via metal coordination,[4,8–10] whereas several others are stable enough to be isolated as such.[1–3,5–7] The interest in the transition-metal coordination chemistry of these ligands stems from the role of the function that can (i) interact directly with the isocyanide[1] or (ii) activate the C–H bond of the adjacent methylene group to produce α-metalated isocyanides[2,7] or metal–carbon bonds.[3,5,6] They then undergo intermolecular nucleophilic attack on the coordinated isocyanide in the presence of 1,3-dipolarophiles or intramolecular migratory rearrangement involving the free $-N{\equiv}C$ group, respectively. It thus appears that the nature of the funtion may dictate the overall properties of the metal–ligand system.

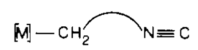
In order to further investigate the synthesis of such ligands, their coordination ability, and their reactivity toward transition metals as related also to the electronic and/or steric effects of the substituent, we have prepared isocyanides of the following structure:



X = Cl, 2-(chloromethyl)phenyl isocyanide ($CN\frown CH_2Cl$)
X = I, 2-(iodomethyl)phenyl isocyanide ($CN\frown CH_2I$)

These ligands, which contain the isocyanide function ($N{\equiv}C$) and the alkyl halide function (CH_2X), can potentially display the reactivity patterns peculiar to each group. As a consequence, their behavior can be depicted as in compounds A–C. For example, species of type A involve simple coordination of the isocyanide end, whereas species of type B might derive from halide displacement by metal carbonyl anions or oxidative addition to metal complexes in low oxidation state. With an appropriate choice of the metal substrate, we have investigated the ability of these ligands to act either as monodentate agents to give "open-chain" mononuclear compounds of the type A and B or as bifunctional entities to give homo- and heterobinuclear species of type C. Of course, derivatives such as A and B can be potential precursors of C. Furthermore, the $CN\frown CH_2X$ ligands are isoelectronic with the corresponding *o*-cyanobenzyl halides whose coordination chemistry has been thoroughly investigated[11] and may well serve

A



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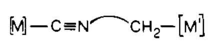

C

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for comparison purposes in establishing general reactivity patterns.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen or argon. *N,N*-Dimethylformamide (DMF) was distilled under N_2 from BaO; tetrahydrofuran (THF), benzene, toluene, diethyl ether, and 1,2-dimethoxyethane (DME) were distilled under N_2 from sodium benzophenone ketyl. 1,2-Dichloroethane (DCE) was dried and distilled under N_2 from CaH_2. Acetone was dried over $CaSO_4$ and degassed 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 597 spectrophotometer. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were run 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 ZAB 2F spectrometer.

Molecular weight measurements were determined on a Knauer osmometer using DCE as solvent.

Melting points were taken on a hot plate apparatus and are uncorrected.

Elemental analyses were performed by the Institute of Analytical Chemistry, University of Padua.

Starting Materials. 2-(Chloromethyl)benzoyl chloride, sodium azide, and lithium aluminum tri-*tert*-butoxyhydride, $LiAlH(O\text{-}t\text{-}Bu)_3$, were purchased from Fluka and used without further purification. The carbonyls $M(CO)_6$ (M = Cr, Mo, W) and $Mn_2(CO)_{10}$ were Alfa products and used as purchased. The complexes $[M(CO)_5I][NEt_4]$[12] (M = Cr, W), $Pt(PPh_3)_2(C_2H_4)$,[13] $Pd_2(dba)_3{\cdot}2CHCl_3$[14] (dba = dibenzylideneacetone), $(COD)PtCl_2$[15] (COD = 1,5-cyclooctadiene), $[MCp(CO)_3]^-$[16] (M = Mo, W; Cp = η^5-C_5H_5), $[Pt(PR_3)Cl_2]_2$[17] (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph), and *trans*-$PtHCl(PPh_3)_2$[18] were prepared according to literature procedures. $PdCl_2(MeCN)_2$ was obtained as a yellow solid in 90% yield by refluxing $PdCl_2$ in acetonitrile until dissolution, followed by precipitation with petroleum ether. Complexes of the type $[Pd(PR_3)Cl_2]_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph) were prepared in about 80% yield by refluxing equimolar amounts of $PdCl_2(MeCN)_2$ and the phosphine for ca. 2–3 h under N_2 in DCE, followed by precipitation with Et_2O/*n*-hexane. *Caution*: All the operations concerning the preparation of the ligands were carried out under a well-ventilated fume hood and with use of disposable gloves. Some compounds, in particular the formamide and the isocyanides, proved to be strong eye and skin irritants.

Synthesis of Ligands. 2-(Chloromethyl)benzoyl Azide. A three-neck round-bottom flask equipped with mechanical stirrer, thermometer, and inlet–outlet for N_2 was charged with DMF (150 mL) and the system cooled to −5 °C with an ice–NaCl bath. 2-(Chloromethyl)benzoyl chloride (15 mL, 20.22 g, 0.107 mol) was added in one portion and the solution vigorously stirred for 1 h. Sodium azide (7.30 g, 0.112 mol) was then added in small portions at such a rate that the temperature never exceeded −5 °C. After the addition was complete, the reaction mixture was stirred for an additional 2 h and then allowed to come to room temperature. It was poured into ice water (250 mL) and the acyl azide extracted with C_6H_6 (3 × 150 mL). The benzene layer was subsequently extracted with ice-cold water (3 × 100 mL) and then dried over anhydrous Na_2SO_4. The yield based on the isocyanate was generally quantitative.

Since the azide was immediately used in the subsequent transformation to the isocyanate, no particular effort was made to isolate it in the routine preparations. However, a pure sample of the azide was obtained as follows. Evaporation to dryness of an aliquot portion of the benzene solution at 5 °C gave an oil that dissolved in Et_2O/*n*-pentane (1:1 mixture, 30 mL) and cooled to −15 °C. White crystals of the azide formed, which are deliquescent and decompose slowly to the isocyanate at room temperature. IR (C_6H_6): $\nu(N_3)$ 2125 s, $\nu(C{=}O)$ 1685 s cm^{-1}. ^1H NMR ($CDCl_3$; Me_4Si): $\delta(CH_2)$ 4.85 s.

2-(Chloromethyl)phenyl Isocyanate. The solution of the azide in C_6H_6 was heated slowly with stirring from room temperature to 80 °C over a period of 4 h and then at reflux for 1 h. It was then taken to dryness under reduced pressure to give 15.0 g (0.089 mol) of the isocyanate as a thick oil; yield 84% (based on the starting benzoyl chloride). IR (C_6H_6): $\nu(NCO)$ 2265 vs cm^{-1}. ^1H NMR ($CDCl_3$; Me_4Si): $\delta(CH_2)$ 4.64 s.

(2-(Chloromethyl)phenyl)formamide. The isocyanate (35.10 g, 0.21 mol) was transferred into a dropping funnel with 200 mL of THF, and the resultant mixture was added slowly (3 h) to a vigorously stirred solution of $LiAlH(O\text{-}t\text{-}Bu)_3$ (68.9 g, 0.27 mol) in THF (300 mL) previously cooled to −15 °C with an ice–NH_4Cl bath. After 3 h of additional stirring, 50% HCOOH (180 mL) was added in 10 min with fast mechanical stirring. The reaction mixture was allowed to reach room temperature, giving a pale yellow clear solution that was taken up with Et_2O (800 mL) and treated with 0.05 N HCl (2 × 300 mL), 1 N HCl (1 × 300 mL), and a saturated solution of Na_2CO_3 (2 × 300 mL). It was then washed with H_2O (3 × 200 mL) and dried over anhydrous $MgSO_4$. The ethereal solution was taken to dryness to yield the crude formamide, which was recrystallized from CH_2Cl_2/Et_2O/*n*-hexane: yield 27 g (76%); mp 90–91 °C. IR (Nujol mull): $\nu(NH)$ 3230 m, $\nu(C{=}O)$ 1660 vs, $\nu(C\text{–}Cl)$ 665 s cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta(CH_2)$ 4.64 s, $\delta(CHO)$ 8.60 s. Anal. Calcd for C_8H_8NClO: C, 56.65; H, 4.75; N, 8.26; Cl, 20.90. Found: C, 56.29; H, 4.91; N, 8.23; Cl, 21.39.

2-(Chloromethyl)phenyl Isocyanide ($CN^\frown CH_2Cl$). A three-neck round-bottom flask equipped with mechanical stirrer, dropping funnel, and inlet–outlet for N_2 was charged with the formamide (14.1 g, 0.083 mol) in DMF (200 mL), and the resultant mixture was cooled to −50 °C with a dry ice–acetone bath. A solution of $SOCl_2$ (6.35 mL, 10.35 g, 0.087 mol) in DMF (50 mL) was added dropwise over a period of 30 min at such a rate that the temperature never exceeded −50 °C. After the addition was complete, the reaction mixture was warmed to −45 °C and anhydrous Na_2CO_3 (19.80 g, 0.18 mol) was added in one portion. The dry ice–acetone bath was removed and the reaction mixture stirred overnight. It was then poured into ice water (500 mL) and extracted with Et_2O (2 × 350 mL). The ethereal layer was extracted with ice water (2 × 300 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation to dryness gave a pale yellow solid that was sublimed at 55 °C (1 × 10^{-2} torr) onto a dry ice-cold probe to give 9.0 g (72.3% yield) of the isocyanide (mp 48–50 °C dec), which was stored under N_2 in the dark at −15 °C. Anal. Calcd for C_8H_6NCl: C, 63.38; H, 3.99; N, 9.24; Cl, 23.38. Found: C, 62.80; H, 3.68; N, 9.02; Cl, 22.78.

2-(Iodomethyl)phenyl Isocyanide ($CN^\frown CH_2I$). To a solution of NaI (37.5 g, 0.25 mol) in acetone (250 mL) was added a solution of $CN^\frown CH_2Cl$ (7.5 g, 0.05 mol) in acetone (70 mL) dropwise over a period of 1 h at room temperature. After the addition was complete, the reaction mixture was stirred for an additional 4 h, giving a white precipitate of NaCl. It was then concentrated under reduced pressure to half its volume, Et_2O (300 mL) was added, and the resultant mixture was quickly filtered on a glass frit and taken to dryness. The residue was dissolved in the minimum amount of benzene, and the resultant mixture was filtered and chromatographed on a column of silica gel (40 × 3 cm) with Et_2O as eluant. The yellow band formed was collected under N_2 and taken to dryness. The pale yellow crude product (10.6 g, 87.2%) could be sublimed (68 °C (1 × 10^{-2} torr)) onto a dry ice-cold probe to give the white isocyanide with only a slight decrease in yield (mp 67–68 °C dec). It was then stored under N_2 in the dark at −15 °C. Anal. Calcd for C_8H_6NI: C, 39.53; H, 2.49; N, 5.76; I, 52.21. Found: C, 39.90; H, 2.41; N, 5.72; I, 51.83.

Preparation of Complexes. $Cr(CO)_5(CN^\frown CH_2Cl)$ (1). To a suspension of $[Cr(CO)_5I][NEt_4]$ (9.0 g, 20.0 mmol) in acetone (130 mL) at 0 °C was added a 0.95 M acetone solution of $AgBF_4$ (22 mL, 20.9 mmol) diluted in acetone (50 mL) dropwise over a period of 20 min. After the addition was complete, the mixture was quickly filtered and the dark orange solution treated dropwise at 0 °C with a solution of $CN^\frown CH_2Cl$ (2.80 g, 18.5 mmol) in acetone (70 mL). After being stirred for an additional 20 min, the yellow-orange solution was allowed to come to room temperature and evaporated to dryness under reduced pressure. The residue was extracted with Et_2O (3 × 100 mL), filtered, taken to dryness, and taken up with the minimum amount of CH_2Cl_2, and the resultant mixture was chromatographed on a silica gel column

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(50 × 3 cm) with Et_2O as eluant. The pale yellow band formed was collected and *n*-hexane (60 mL) added. On concentration and cooling, pale yellow crystals of the compound were obtained, which were filtered off and dried under vacuum: mp 73–75 °C; yield 5.1 g or 80.2% (based on the isocyanide). Anal. Calcd for $C_{13}H_6NO_5ClCr$: C, 45.43; H, 1.76; N, 4.08; Cl, 10.32. Found: C, 45.80; H, 1.79; N, 4.12; Cl, 9.83.

$W(CO)_5(CN^\frown CH_2Cl)$ (2). This compound was prepared by a procedure similar to that used for complex **1** starting from $[W(CO)_5I][NEt_4]$ (5.81 g, 10.0 mmol), 0.95 M $AgBF_4$ (10 mL, 10.5 mmol), and $CN^\frown CH_2Cl$ (1.45 g, 9.57 mmol): yield 3.2 g (70.3%); mp 72–73 °C dec. Anal. Calcd for $C_{13}H_6NO_5ClW$: C, 32.80: H, 1.27; N, 2.94; Cl, 7.45. Found: C, 33.07; H, 1.32; N, 2.98; Cl, 7.21.

$Cr(CO)_5(CN^\frown CH_2I)$ (3). Method A. This procedure was similar to that reported for **1** starting from $[Cr(CO)_5I][NEt_4]$ (4.53 g, 10.0 mmol), 1.0 M $AgBF_4$ (10 mL, 10.0 mmol), and $CN^\frown CH_2I$ (2.43 g, 10.0 mmol): yield of the yellow product 3.5 g (82%); mp 98–99 °C. Anal. Calcd for $C_{13}H_6NO_5ICr$: C, 35.88; H, 1.39; N, 3.22; I, 29.16. Found: C, 36.04; H, 1.48; N, 3.30; I, 28.83.

Method B. Complex **1** (3.5 g, 10.2 mmol) was reacted with a solution of NaI (9.0 g, 60.0 mmol) in acetone (90 mL) at room temperature overnight. The reaction mixture was taken to dryness and extracted with C_6H_6 (80 mL). The benzene solution was concentrated to small volume and chromatographed on a silica gel column (40 × 3 cm) with Et_2O as eluant. The yellow band developed was collected and evaporated to small volume and *n*-hexane (30 mL) added. On cooling to −10 °C, a yellow precipitate of the compound formed; yield 3.8 g (85.6%).

$W(CO)_5(CN^\frown CH_2I)$ (4). This compound was prepared by both methods A and B as described for **3** with 73 or 65% yield, respectively; mp 99–100 °C. Anal. Calcd for $C_{13}H_6NO_5IW$: C, 27.54; H, 1.06; N, 2.47; I, 22.38. Found: C, 27.59; H, 1.00; N, 2.40; I, 21.92.

***cis*-$MCl_2(PR_3)(CN^\frown CH_2Cl)$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph; M = Pd (5–7), Pt (8–10)).** All these complexes, which analyzed well for the proposed structures, were prepared by a standard procedure that is described for compound **6**. A solution of $CN^\frown CH_2Cl$ (0.75 g, 4.95 mmol) in C_6H_6 (30 mL) was added dropwise with stirring over a period of 30 min to a suspension of $[Pd(PMePh_2)Cl_2]_2$ (1.83 g, 2.42 mmol) in C_6H_6 (30 mL) at room temperature. A yellow solution was obtained from which an off-white solid began to precipitate after 1 h. The reaction mixture was reduced to small volume and Et_2O (40 mL) added. The solid was filtered off and recrystallized from CH_2Cl_2/Et_2O: yield 1.9 g (79.8%); mp 168–169 °C dec. Anal. Calcd for $C_{21}H_{19}NCl_3PPd$: C, 47.67; H, 3.62; N, 2.65; Cl, 20.10. Found: C, 48.14; H, 3.63; N, 2.51; Cl, 19.81.

The melting points of the other complexes are as follows: **5**, 199–201 °C dec; **7**, 151–152 °C dec; **8**, 208–210 °C; **9**, 157–158 °C: **10**, 135–136 °C.

***cis*-$PdCl_2(CN^\frown CH_2Cl)_2$ (11).** To a solution of $PdCl_2(MeCN)_2$ (1.3 g, 5.0 mmol) in C_6H_6 (30 mL) was added a solution of $CN^\frown CH_2Cl$ (1.54 g, 10.2 mmol) in C_6H_6 (50 mL) dropwise at room temperature with stirring over a period of 30 min. The reaction mixture was stirred for an additional 2 h. Et_2O (100 mL) was added and the white solid filtered off and dried under vacuum: yield 4.2 g (87.5%); mp 195–198 °C dec. Anal. Calcd for $C_{16}H_{12}N_2Cl_4Pd$: C, 39.99; H, 2.52; N, 5.83; Cl, 29.51. Found: C, 40.18; H, 2.54; N, 5.77; Cl, 29.30.

***cis*-$PtCl_2(CN^\frown CH_2Cl)_2$ (12).** This compound was prepared as reported for **11** starting from $(COD)PtCl_2$ (0.37 g, 1.0 mmol) and $CN^\frown CH_2Cl$ (0.31 g, 2.04 mmol): yield 0.46 g (80.8%); mp 214–215 °C dec. Anal. Calcd or $C_{16}H_{12}N_2Cl_4Pt$: C, 33.76; H, 2.12; N, 4.92; Cl, 24.91. Found: C, 34.10; H, 2.12; N, 4.97; Cl, 24.64.

***trans*-$PtCl(PPh_3)_2(CHN^\frown CH_2Cl)$ (13).** A solution of $CN^\frown CH_2Cl$ (0.34 g, 2.25 mmol) in C_6H_6 (15 mL) was added dropwise over a period of 1 h to a suspension of *trans*-$PtHCl(PPh_3)_2$ (1.7 g, 2.25 mmol) in C_6H_6 (20 mL). The solution turned gradually orange-yellow and was stirred overnight. It was then concentrated to ca. 10 mL, Et_2O (40 mL) was added and the resultant mixture was filtered. Addition of MeOH (30 mL) and evaporation under reduced pressure gave a cream solid, which was filtered and recrystallized from CH_2Cl_2/MeOH: yield 0.8 g (39%); mp 175–176 °C dec. Anal. Calcd for $C_{44}H_{37}NCl_2P_2Pt$: C, 58.22; H, 4.10; N, 1.54; Cl, 7.81. Found: C, 57.77; H, 4.16; N, 1.37; Cl, 6.93.

$Cr(CO)_5(CN^\frown CH_2NH$-*p*-$C_6H_4Me)$ (14). A solution of **3** (0.43 g, 1.0 mmol) in DCE (10 mL) was stirred with *p*-toluidine (0.53 g, 5.0 mmol) at room temperature for 18 h. The solid formed (i.e. *p*-$MeC_6H_4NH_3^+I^-$) was filtered off and the solution taken to dryness. The residue was dissolved in the minimum amount of CH_2Cl_2, and the mixture was chromatographed on a silica gel column (20 × 2 cm) with Et_2O as eluant. The pale yellow band was collected and evaporated to a small volume. When *n*-hexane (20 mL) was added, the product precipitated as a white solid, which was filtered and dried under vacuum: yield 0.22 g (53%); mp 110–112 °C. Anal. Calcd for $C_{20}H_{14}N_2O_5Cr$: C, 57.97; H, 3.40; N, 6.76. Found: C, 58.29; H, 3.51; N, 6.86.

$W(CO)_5(CN^\frown CH_2NH$-*p*-$C_6H_4Me)$ (15). This compound was obtained as for **14** starting from **4** (0.34 g, 0.61 mmol) and *p*-toluidine (0.32 g, 3.1 mmol) in DCE (15 mL): yield 0.15 g (45%); mp 122–123 °C. Anal. Calcd for $C_{20}H_{14}N_2O_5W$: C, 43.98; H, 2.58; N, 5.13. Found: C, 43.31; H, 2.53; N, 5.07.

$Cr(CO)_5(CN^\frown CH_2)MoCp(CO)_3$ (16). To a stirred solution of **3** (1.2 g, 2.75 mmol) at −78 °C was added a solution of $MoCp(CO)_3^-$ (3.3 mmol) in DME (15 mL) via a cannula. The reaction mixture was stirred at low temperature for 1 h and then slowly warmed to room temperature and stirred overnight. The orange solution was taken to dryness and extracted with C_6H_6/Et_2O (1:1 mixture, 100 mL), filtered, and evaporated to dryness. The residue was dissolved in the minimum amount of CH_2Cl_2, and the resultant solution was chromatographed on Florisil with Et_2O as eluant. The yellow band was collected and concentrated to ca. 20 mL. When *n*-hexane (40 mL) was added and the mixture was cooled to −15 °C, a yellow crystalline solid precipitated. It was filtered off and dried in vacuo: yield 1.2 g (79%) (based on complex **3**): mp 119–120 °C. Anal. Calcd for $C_{21}H_{11}NO_8CrMo$: C, 45.59; H, 2.00; N, 2.53. Found: C, 45.74; H, 1.98; N, 2.38. The mass spectrum showed M^+ at *m/e* 555 (for ^{52}Cr and ^{98}Mo) and peaks for $[M - n(CO)]^+$ (n = 1–8).

$W(CO)_5(CN^\frown CH_2)MoCp(CO)_3$ (17). A procedure analogous to that described above using compound **4** (1.05 g, 1.85 mmol) and $MoCp(CO)_3^-$ (2.0 mmol) gave the product (0.92 g (74.3%)) as yellow crystals (mp 121–122 °C). Anal. Calcd for $C_{21}H_{11}NO_8WMo$: C, 36.81; H, 1.62; N, 2.04. Found: C, 36.30; H, 1.61; N, 2.02. The mass spectrum showed M^+ at *m/e* 687 (for ^{184}W and ^{98}Mo) and peaks for $[M - n(CO)]^+$ (n = 1–8).

$W(CO)_5(CN^\frown CH_2)WCp(CO)_3$ (18). The same procedure as above for **16** was used; starting from complex **4** (1.02 g, 1.80 mmol) and $WCp(CO)_3^-$ (2.1 mmol) gave the compound as yellow crystals: 0.8 g (51.7%); mp 125–126 °C. Anal. Calcd for $C_{21}H_{11}NO_8W_2$: C, 32.63; H, 1.43; N, 1.81. Found: C, 33.30; H, 1.42; N, 1.81. The mass spectrum showed M^+ at *m/e* 773 (for ^{184}W) and peaks for $[M - n(CO)]^+$ (n = 1–8).

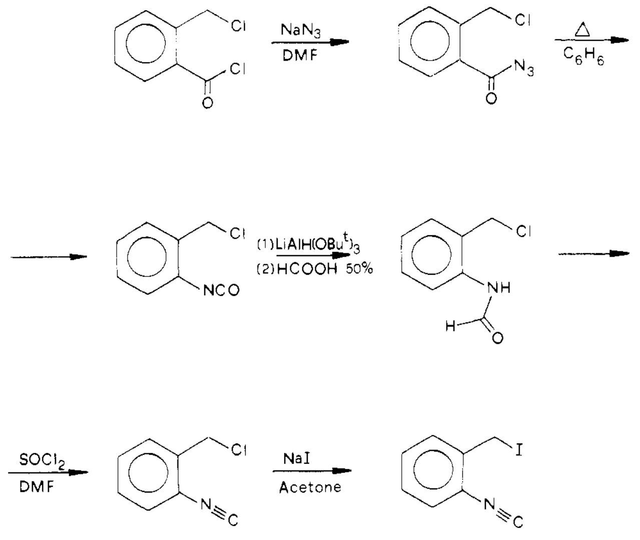
$W(CO)_5(CN^\frown CH_2)Mn(CO)_5$ (19). Na/Hg prepared from Na (1.0 g) and Hg (10 mL) in THF (30 mL) was treated with a solution of $Mn_2(CO)_{10}$ (1.0 g, 2.8 mmol) in THF (20 mL). The mixture was vigorously stirred for 3 h, filtered through Celite, and treated dropwise over a period of 30 min at room temperature with a solution of complex **4** (2.8 g, 5.0 mmol) in THF (50 mL). The resulting red-orange solution was stirred overnight and then taken to dryness and treated with Et_2O (20 mL). The insoluble cream solid was filtered and recrystallized from CH_2Cl_2/*n*-hexane to yield the product: 0.7 g (22%); mp 196–197 °C. Anal. Calcd for $C_{18}H_6NO_{10}WMn$: C, 34.04; H, 0.95; N, 2.20. Found: C, 34.59; H, 1.17; N, 2.17. The mass spectrum showed M^+ at *m/e* 634 (for ^{183}W and ^{55}Mn) and peaks for $[M - n(CO)]^+$ (n = 5–10).

$Cr(CO)_5(CN^\frown CH_2)$-*trans*-$PtI(PPh_3)_2$ (20). A solution of complex **3** (0.97 g, 2.0 mmol) in C_6H_6 (80 mL) at 5 °C was reacted with $Pt(PPh_3)_2(C_2H_4)$ (1.5 g, 2.0 mmol). The reaction mixture was warmed to room temperature and stirred overnight. It was then taken to dryness and chromatographed on a short column of silica gel (10 × 3 cm) with CH_2Cl_2 as eluant. The yellow band was collected and taken to dryness and the residue recrystallized twice from toluene-/*n*-hexane to give pale yellow crystals of the product: yield 1.2 g (51.9%); mp 174–175 °C dec. Anal. Calcd for $C_{49}H_{36}NO_5IP_2CrPt$: C, 50.97; H, 3.14; N, 1.21; I, 10.99. Found: C, 50.32; H, 3.17; N, 0.93; I, 11.25.

$W(CO)_5(CN^\frown CH_2)$-*trans*-$PtI(PPh_3)_2$ (21). This compound was prepared with a procedure analogous to that described for **20** starting from **4** (1.13 g, 2.0 mmol) and $Pt(PPh_3)_2(C_2H_4)$ (1.5 g, 2.0 mmol): yield 1.3 g (50.5%); mp 196–198 °C dec. Anal. Calcd for $C_{49}H_{36}NO_5IP_2WPt$: C, 45.74; H, 2.82; N, 1.08; I, 9.86. Found: C, 45.72; H, 2.83; N, 0.95; I, 10.05. Mol wt: calcd, 1286; found, 1279.

$Cr(CO)_5(CN^\frown CH_2)$-*trans*-$PdI(PPh_3)_2$ (22). To a solution of $Pd_2(dba)_3{\cdot}2CHCl_3$ (1.03 g, 1.0 mmol) in toluene (100 mL) was added PPh_3 (1.1 g, 4.2 mmol) and the mixture stirred at room temperature for 3 h. The solution was then cooled to −15 °C and complex **3** (0.87

Scheme I



g, 2.0 mmol) added. The reaction mixture was stirred at low temperature for 1 h and then allowed to reach room temperature and stirred for 3 days. It was then taken to dryness and the residue dissolved in the minimum amount of CH_2Cl_2. The resulting solution was chromatographed on a short column of silica gel (10 × 3 cm). The eluted deep orange solution was concentrated under reduced pressure, and orange crystals were formed on addition of Et_2O: yield 0.8 g (37.5%); mp 130–133 °C dec. Anal. Calcd for $C_{49}H_{36}NO_5P_2ICrPd$: C, 55.20; H, 3.40; N, 1.31; I, 11.90. Found: C, 54.82; H, 3.28; N, 1.23; I. 11.45.

[PtI(PPh$_3$)($\mathrm{CN{\frown}CH_2}$)]$_2$ (23). To a solution of $Pt(PPh_3)_2(C_2H_4)$ (1.4 g, 1.87 mmol) in toluene (100 mL) previously cooled to −15 °C was added in one portion solid $\mathrm{CN{\frown}CH_2I}$ (0.48 g, 2.1 mmol). The reaction mixture was stirred for 1 h and then slowly warmed to room temperature and stirred for an additional 15 h. It was filtered and concentrated to ca. 20 mL and Et_2O (150 mL) added. After filtration, the orange solution was concentrated to ca. 30 mL and *n*-hexane (60 mL) added. The organce precipitate formed was filtered and dissolved in the minimum amount of C_6H_6 and the solution passed through a short column (1 × 7 cm) of Florisil. The eluted pale yellow solution was treated with MeOH to give a white solid, which was filtered and dried in vacuo: yield 0.6 g (42.8%); mp 163–165 °C dec. Anal. Calcd for $C_{26}H_{21}NIPPt$: C, 44.59; H, 3.02; N, 1.99; I, 18.12. Found: C, 44.62; H, 3.07; N, 1.71; I, 18.45. Mol wt: calcd, 1400; found, 1357.

Results and Discussion

Synthesis of Ligands. The ligands 2-(chloromethyl)- and 2-(iodomethyl)phenyl isocyanide, which will be referred to as $\mathrm{CN{\frown}CH_2Cl}$ and $\mathrm{CN{\frown}CH_2I}$ throughout, have been prepared as shown in Scheme I.

The first stage involves conversion of the acyl chloride to acyl azide in DMF, which has been made selective by formation of an acyl chloride–DMF complex.[19] Subsequent Curtius rearrangement yields the corresponding isocyanate, which is then reduced to the formamide by LiAlH(O-*t*-Bu)$_3$ in THF at −15 °C, followed by treatment with HCOOH (50%), as reported for the reduction of other isocyanates.[20] The formamide is then dehydrated with $SOCl_2$/DMF to yield the isocyanide $\mathrm{CN{\frown}CH_2Cl}$ with an overall yield of ca. 45%. The iodide $\mathrm{CN{\frown}CH_2I}$ is obtained from the parent chloride by metathesis with NaI in acetone (yield ca. 85%).

These isocyanides are white, crystalline, foul-smelling, eye- and skin-irritating solids that can be easily sublimed under reduced pressure at 55–65 °C. They are soluble in most common organic solvents and are better stored under nitrogen in the cold. Their characterization has been achieved by elemental analysis and IR, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy (see Experimental Section and Tables I–III). Typical IR features (cm^{-1}) are the $\nu(N{\equiv}C)$ (CH_2Cl_2: X = Cl, 2124 s; X = I, 2123 s) and ν(C–X) (Nujol mull: X = Cl, 665 s; X = I, 570 s) stretching frequencies (Table I).

The CH_2X methylene protons show up in the ^1H NMR spectra as sharp singlets at δ 4.71 (X = Cl) and δ 4.51 (X = I) (Table II). The $^{13}C\{^1H\}$ NMR spectra (of solutions containing $Cr(acac)_3$ as relaxation reagent) (Table III) display the isocyanide carbon absorptions at ca. 168 ppm as weak signals broadened by ^{14}N coupling. The CH_2X signals undergo the usual upfield shift on going from chloride to iodide.[21] As regards the phenyl-ring carbons, only the resonances of carbons bound to the –NC and CH_2X groups could be assigned with certainty. The former is also broadened by ^{14}N coupling and located at higher field than the latter (cf. *C*–CH_2Cl in benzyl chloride at δ 137.3). The other ring carbons generally resonate in the range 130–126 ppm.

Reactions Involving the Isocyanide Function. Mononuclear Complexes. The coordinating ability of the isocyano ligands $\mathrm{CN{\frown}CH_2X}$ has been tested by carrying out a series of reactions that are known to yield stable metal complexes with the corresponding monodentate isocyanides. These reactions, which involve only the isocyano function, are outlined in Schemes II (X = Cl) and III (X = I).

The substituted carbonyl derivatives **1–4** are produced with 70–80% yield and are soluble in chlorinated solvents and aromatic hydrocarbons. The iodide derivatives **3** and **4** have been obtained with comparable yields from their parent chlorides also by metathesis with excess NaI in acetone. The complexes **1–4** were characterized by comparison of their IR spectral features in the NC and CO stretching regions (Table I) with those reported for analogous carbonyl–isocyanide complexes.[22–24] The ^1H and ^{13}C NMR spectra (Tables II and III) are also consistent with their formulation.[24,25]

The mononuclear isocyanide derivatives *cis*-$MCl_2(PR_3)$($\mathrm{CN{\frown}CH_2Cl}$) (**5–10**) are formed with 70–80% yield. Selected diagnostic IR bands (M–Cl[26] and NC[27,28] stretchings) are listed in Table I. Complexes **5–10** display a high reactivity of the isocyanide toward nucleophiles: e.g., they react with aromatic amines to yield amino–carbene complexes according to mechanistic pathways that are being studied.[29]

The halide bridge splitting in $[Pt(PMePh_2)Cl_2]_2$ by $\mathrm{CN{\frown}CH_2I}$ (Scheme III) leads to a mixture of products containing PtClI($PMePh_2$)($\mathrm{CN{\frown}CH_2Cl}$) (**9a**, major product), *cis*-$PtCl_2(PMePh_2)$($\mathrm{CN{\frown}CH_2Cl}$) (**9**), and $PtI_2(PMePh_2)$($\mathrm{CN{\frown}CH_2I}$) (**9b**). It appears that chloride–iodide exchange reactions have involved both the central metal and the *o*-CH_2I group in the isocyanide. Identification of the mixture of these products is based on IR and NMR spectral data.[30]

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Table I. IR Spectral Data

compd	solvent	ν(N≡C), cm^{-1}	ν(C≡O), cm^{-1}	other,[a] cm^{-1}
o-ClCH$_2$C$_6$H$_4$NC (CN$\frown$CH$_2$Cl)	CH$_2$Cl$_2$	2124 s		ν(C–Cl) 665 s
o-ICH$_2$C$_6$H$_4$NC (CN$\frown$CH$_2$I)	CH$_2$Cl$_2$	2123 s		ν(C–I) 570 s
Cr(CO)$_5$(CN$\frown$CH$_2$Cl) (**1**)	CH$_2$Cl$_2$	2134 w	2052 m, 1998 vw, sh, 1962 vs, br	
W(CO)$_5$(CN$\frown$CH$_2$Cl) (**2**)	CH$_2$Cl$_2$	2136 w	2053 m, 1998 vw, sh, 1955 vs, br	
Cr(CO)$_5$(CN$\frown$CH$_2$I) (**3**)	CH$_2$Cl$_2$	2135 w	2054 m, 1994 vw, sh, 1956 vs, br	
W(CO)$_5$(CN$\frown$CH$_2$I) (**4**)	CH$_2$Cl$_2$	2134 w	2051 m, 1995 vw, sh, 1955 vs, br	
cis-PdCl$_2$(PPh$_3$)(CN$\frown$CH$_2$Cl) (**5**)	*a*	2215 s (2209 s)[b]		ν(C–Cl) 675 m, ν(Pd–Cl) 345 m, 300 m–s
cis-PdCl$_2$(PMePh$_2$)(CN$\frown$CH$_2$Cl) (**6**)	*a*	2205 s (2206 s)[b]		ν(C–Cl) 668 m, ν(Pd–Cl) 345 m, 298 m–s
cis-PdCl$_2$(PMe$_2$Ph)(CN$\frown$CH$_2$Cl) (**7**)	*a*	2195 s (2204 s)[b]		ν(C–Cl) 672 m, ν(Pd–Cl) 340 m–w, 288 m–s
cis-PtCl$_2$(PPh$_3$)(CN$\frown$CH$_2$Cl) (**8**)	*a*	2198 s (2201 s)[b]		ν(C–Cl) 673 m, ν(Pt–Cl) 350 m, 300 m–s
cis-PtCl$_2$(PMePh$_2$)(CN$\frown$CH$_2$Cl) (**9**)	*a*	2190 s (2198 s)[b]		ν(C–Cl) 670 m, ν(Pt–Cl) 345 m, 300 m
cis-PtCl$_2$(PMe$_2$Ph)(CN$\frown$CH$_2$Cl) (**10**)	*a*	2185 s (2196 s)[b]		ν(C–Cl) 670 m, ν(Pt–Cl) 338 m–s, 295 s
cis-PdCl$_2$(CN$\frown$CH$_2$Cl)$_2$ (**11**)	*a*	2235 s, 2215 s		ν(C–Cl) 670 s, ν(Pd–Cl) 350 s, 330 s
cis-PtCl$_2$(CN$\frown$CH$_2$Cl)$_2$ (**12**)	*a*	2235 s, 2205 s		ν(C–Cl) 675 m–s, ν(Pt–Cl) 350 m, 325 m
trans-PtCl(PPh$_3$)$_2$(CHN$\frown$CH$_2$Cl) (**13**)	*a*			ν(C–Cl) 672 m, ν(C=N) 1562 s, ν(Pt–Cl) 270 m
Cr(CO)$_5$(CN$\frown$CH$_2$NH-*p*-C$_6$H$_4$Me) (**14**)	CH$_2$Cl$_2$	2143 w	2049 m, 1995 w, sh, 1954 vs	ν(N–H) 3415 w
W(CO)$_5$(CN$\frown$CH$_2$NH-*p*-C$_6$H$_4$Me) (**15**)	CH$_2$Cl$_2$	2144 w	2059 m, 1990 vw, sh, 1951 vs	ν(N–H) 3420 w
Cr(CO)$_5$(CN$\frown$CH$_2$)MoCp(CO)$_3$ (**16**)	CH$_2$Cl$_2$	2146 w	2061 m, 2026 m, 1995 vw, sh, 1953 vs, br, 1930 sh	
	n-hexane	2139 w	2061 m, 2031 m, 1998 w, 1965 s, 1952 s, 1947 m	
W(CO)$_5$(CN$\frown$CH$_2$)MoCp(CO)$_3$ (**17**)	CH$_2$Cl$_2$	2145 w	2062 m, 2023 m, 1949 vs, br, 1929 sh	
	n-hexane	2138 w	2061 m, 2027 m, 1993 w, 1962 vs, 1949 vs, 1937 s	
W(CO)$_5$(CN$\frown$CH$_2$)WCp(CO)$_3$ (**18**)	CH$_2$Cl$_2$	2144 w	2069 m, 2026 m, 1995 vw, 1950 vs, br, 1920 sh	
	n-hexane	2141 w	2064 m, 2028 m, 1993 w, 1960 vs, 1942 s, 1927 m	
W(CO)$_5$(CN$\frown$CH$_2$)Mn(CO)$_5$ (**19**)	CH$_2$Cl$_2$	2137 w	2107 w, 2057 m, 2019 s, 1997 m, 1949 vs	
Cr(CO)$_5$(CN$\frown$CH$_2$)-*trans*-PtI(PPh$_3$)$_2$ (**20**)	CH$_2$Cl$_2$	2146 w	2061 m, 1990 vw, sh, 1951 vs	
W(CO)$_5$(CN$\frown$CH$_2$)-*trans*-PtI(PPh$_3$)$_2$ (**21**)	CH$_2$Cl$_2$	2144 w	2061 m, 1990 vw, sh, 1948 vs	
Cr(CO)$_5$(CN$\frown$CH$_2$)-*trans*-PdI(PPh$_3$)$_2$ (**22**)	CH$_2$Cl$_2$	2144 w	2059 m, 1995 vw, sh, 1952 vs	
[PtI(PPh$_3$)(CN$\frown$CH$_2$)]$_2$ (**23**)	*a*	2170 s		

[a] Nujol mull; vs = very strong, s = strong, m = medium, vw = very weak, w = weak, sh = shoulder, br = broad. [b] CH$_2$Cl$_2$.

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

compd	^1H NMR δ(CH_2)	^1H NMR δ(other)	$^{31}P\{^1H\}$ NMR δ(P)
o-$ClCH_2C_6H_4NC$ ($CN\frown CH_2Cl$)	4.71 s		
o-$ICH_2C_6H_4NC$ ($CN\frown CH_2I$)	4.52 s		
$Cr(CO)_5(CN\frown CH_2Cl)$ (1)	4.69 s		
$W(CO)_5(CN\frown CH_2Cl)$ (2)	4.70 s		
$Cr(CO)_5(CN\frown CH_2I)$ (3)	4.51 s		
$W(CO)_5(CN\frown CH_2I)$ (4)	4.49 s		
cis-$PdCl_2(PPh_3)(CN\frown CH_2Cl)$ (5)	4.58 s		27.80 s
cis-$PdCl_2(PMePh_2)(CN\frown CH_2Cl)$ (6)	4.59 s	2.42 d[b]	19.10 s
cis-$PdCl_2(PMe_2Ph)(CN\frown CH_2Cl)$ (7)	4.62 s	2.12 d[c]	9.77 s
cis-$PtCl_2(PPh_3)(CN\frown CH_2Cl)$ (8)	4.55 s		8.58 s (^1J(P-Pt) = 3336)
cis-$PtCl_2(PMePh_2)(CN\frown CH_2Cl)$ (9)	4.54 s	2.43 d[d]	−2.05 s (^1J(P-Pt) = 3227)
cis-$PtCl_2(PMe_2Ph)(CN\frown CH_2Cl)$ (10)	4.59 s	2.10 d[e]	−13.24 s (^1J(P-Pt) = 3128)
cis-$PdCl_2(CN\frown CH_2Cl)_2$ (11)	4.80 s		
cis-$PtCl_2(CN\frown CH_2Cl)_2$ (12)	4.75 s		
trans-$PtCl(PPh_3)(CHN\frown CH_2Cl)$ (13)	4.10 s (syn)	9.61 t[f]	21.07 s (^1J(P-Pt) = 3180)
	3.33 s (anti)	9.89 t[g]	
$Cr(CO)_5(CN\frown CH_2NH$-*p*-$C_6H_4Me)$ (14)	4.48 s	2.21 s,[h] 4.10 br[i]	
$W(CO)_5(CN\frown CH_2NH$-*p*-$C_6H_4Me)$ (15)	4.46 s	2.20 s,[h] 4.10 br[i]	
$Cr(CO)_5(CN\frown CH_2)MoCp(CO)_3$ (16)	2.84 s	5.37 s[j]	
$W(CO)_5(CN\frown CH_2)MoCp(CO)_3$ (17)	2.85 s	5.39 s[j]	
$W(CO)_5(CN\frown CH_2)WCp(CO)_3$ (18)	2.92 s[k]	5.49 s[j]	
$W(CO)_5(CN\frown CH_2)Mn(CO)_5$ (19)	2.39 s		
$Cr(CO)_5(CN\frown CH_2)$-*trans*-$PtI(PPh_3)_2$ (20)	2.29 t[l]		23.9 s (^1J(P-Pt) = 3018)
$W(CO)_5(CN\frown CH_2)$-*trans*-$PtI(PPh_3)_2$ (21)	2.26 t[m]		23.92 s (^1J(P-Pt) = 3016)
$Cr(CO)_5(CN\frown CH_2)$-*trans*-$PdI(PPh_3)_2$ (22)	2.34 t[n]		27.43 s[o]
$[PtI(PPh_3)(CN\frown CH_2)]_2$ (23)	3.74 d[p]		12.82 s (^1J(P-Pt) = 1697)

[a] Spectra recorded in CD_2Cl_2; proton chemical shifts reported from tetramethylsilane by taking the chemical shift of dichloromethane-*d*$_2$ as +5.32 ppm; phosphorus chemical shifts referenced to external H_3PO_4 (85%); *J* in Hz; s = singlet, d = doublet, t = triplet, br = broad. [b] PMe (^2J(H-P) = 12.6). [c] PMe (^2J(H-P) = 12.8). [d] PMe (^2J(H-P) = 12.0, ^3J(H-Pt) = 35.0). [e] PMe (^2J(H-P) = 12.1, ^3J(H-Pt) = 37.4). [f] CH (^2J(H-Pt) = 74.5, ^3J(H-P) = 8.0). [g] CH (^2J(H-Pt) = 67.5, ^3J(H-P) = 6.5). [h] Me. [i] NH. [j] Cp (η^5-C_5H_5). [k] ^2J(H-W) = 3.4. [l] ^2J(H-Pt) = 85.5, ^3J(H-P) = 8.0. [m] ^2J(H-Pt) = 86.0, ^3J(H-P) = 8.2. [n] At −40 °C, ^3J(H-P) = 7.5. [o] At −40 °C. [p] ^2J(H-Pt) = 88.3, ^3J(H-P) = 10.4.

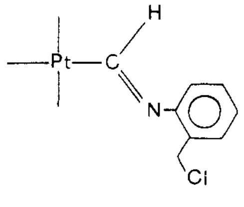
Table III. $^{13}C\{^1H\}$ NMR Spectral Data for the Ligands and Their Carbonyl Complexes[a]

compd	δ NC	δ CH_2	δ C_6H_4	δ Cp	δ CO
o-$ClCH_2C_6H_4NC$ ($CN\frown CH_2Cl$)	168.0	41.1	133.1, 129.6, 129.3, 129.1, 126.6, 125.1		
o-$ICH_2C_6H_4NC$ ($CN\frown CH_2I$)	168.6	−1.5	135.0, 129.4, 128.5, 126.8, 120.6		
$Cr(CO)_5(CN\frown CH_2Cl)$ (1)	176.7	41.6	133.7, 130.1, 129.6, 129.0, 127.1, 126.3		215.9,[b] 213.9[c]
$W(CO)_5(CN\frown CH_2Cl)$ (2)	156.8	41.6	134.0, 130.0, 129.5, 129.1, 126.3		195.3,[b] 193.2[c,d]
$Cr(CO)_5(CN\frown CH_2I)$ (3)	175.4	−1.8	135.4, 129.4, 129.0, 128.8, 127.2, 126.5		215.8,[b] 214.0[c]
$W(CO)_5(CN\frown CH_2I)$ (4)	156.6	−2.0	135.6, 129.2, 129.1, 129.0, 128.7, 126.5		195.1,[b] 193.2[c,d]
$Cr(CO)_5(CN\frown CH_2)MoCp(CO)_3$ (16)	171.2	−3.1	148.8, 128.5, 128.1, 126.1, 123.6	93.0	238.0,[e] 227.6,[f] 216.4,[g] 214.3[h]
$W(CO)_5(CN\frown CH_2)MoCp(CO)_3$ (17)	*i*	−3.0	149.4, 128.8, 128.1, 126.3, 123.7, 123.5	93.1	238.0,[e] 227.7,[f] 195.9,[j] 193.8[d,k]
$W(CO)_5(CN\frown CH_2)WCp(CO)_3$ (18)	*i*	−15.0	149.6, 128.8, 128.1, 126.3, 123.8	91.7	226.5,[l] 218.0,[m] 195.9,[j] 193.8[k]
$W(CO)_5(CN\frown CH_2)Mn(CO)_5$ (19)	*i*	4.4	149.0, 129.1, 127.6, 124.0, 123.9		210.0,[n] 196.0,[j] 199.7[d,k]

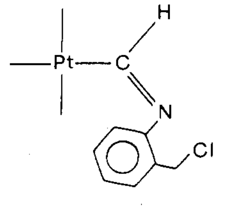
[a] Spectra run in $CDCl_3$ as solvent; chemical shifts reported from Me_4Si by taking the chemical shift of chloroform-*d* as +77.0 ppm; *J* in Hz. [b] Trans CO. [c] Cis CO. [d] ^1J(^{183}W-cis CO) = 126. [e] $Mo(CO)_3$ unit; CO trans to CH_2. [f] $Mo(CO)_3$ unit; CO cis to CH_2. [g] $Cr(CO)_5$ unit; trans CO. [h] $Cr(CO)_5$ unit; cis CO. [i] Resonance not observed. [j] $W(CO)_5$ unit; trans CO. [k] $W(CO)_5$ unit; cis CO. [l] $W(CO)_3$ unit; CO trans to CH_2. [m] $W(CO)_3$ unit; CO cis to CH_2. [n] $Mn(CO)_5$ unit, broad signal.

The bis(isocyanide) complexes **11** and **12** are produced with 80–90% yield. Owing probably to the mutual influence of cis isocyanides, the ν(NC) stretchings undergo the highest increase on coordination observed in this series of functional isocyanide complexes, suggesting a very high electrophilic character for the isocyanide carbon[26a] (Table I).

These functionalized isocyanides undergo other typical reactions of the NC group such as insertion into the Pt–H bond yielding formimidoyl complexes. The insertion product **13** shows IR and NMR features (Tables I–III) typical of these derivatives, inclusive of syn–anti isomerism.[31]



syn



anti

Reactions Involving the Halomethyl Function. Binuclear Complexes. The mononuclear complexes **3** and **4** display a

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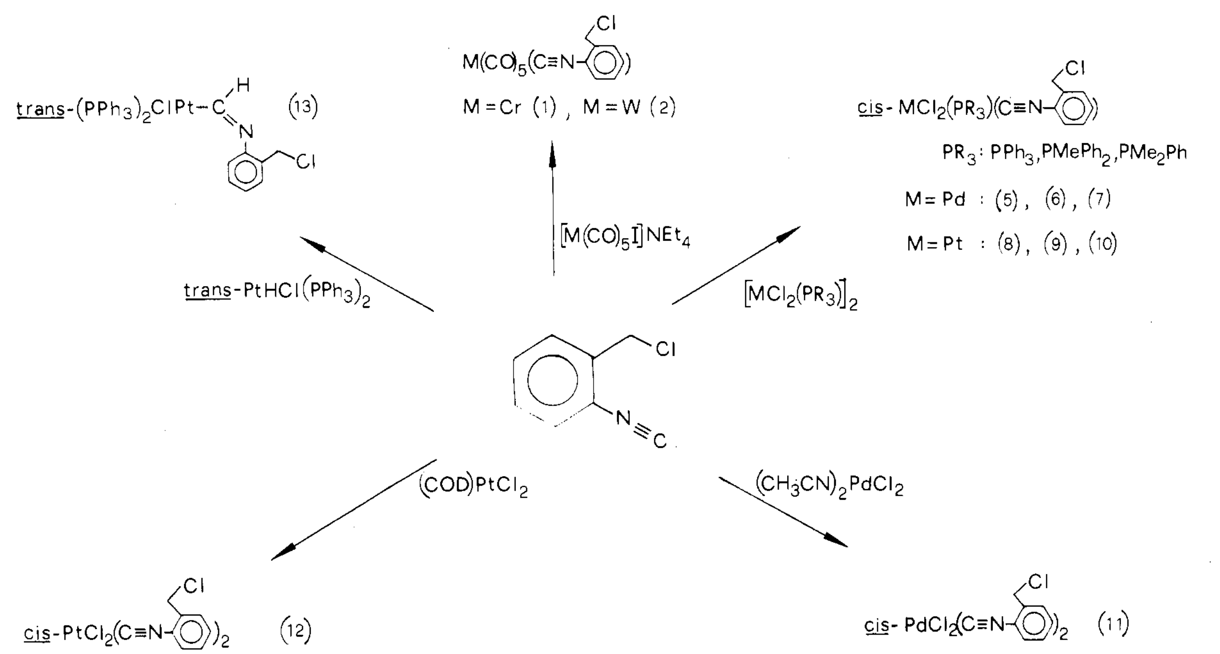
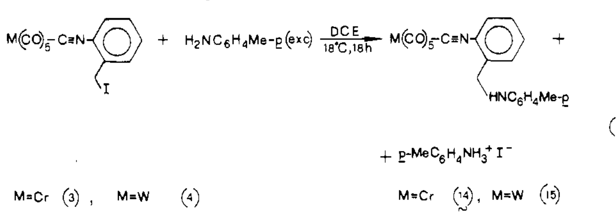
(30) Compound **9**: its presence is confirmed by comparison with data of an independently prepared sample (see Tables I and II and Experimental Section). Compound **9a**: IR (Nujol) ν(N≡C) 2185 s, ν(C–Cl) 673 m, ν(Pt–Cl) 338 m cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.55 s (CH_2), δ 2.34 d (P–CH_3, ^2J(H–P) = 12.0 Hz, ^3J(H–Pt) = 35.2 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2/H_3PO_4 (85%)) δ 0.45 (^1J(P–Pt) = 3089 Hz). Compound **9b**: IR (Nujol) ν(N≡C) 2190 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.49 s (CH_2), δ 2.68 d (P–CH_3, ^2J(H–P) = 11.6 Hz, ^3J(H–Pt) = 37.8 Hz; $^{31}P\{^1H\}$ NMR (CD_2Cl_2/H_3PO_4 (85%)) δ −5.48 (^1J(P–Pt) = 3063 Hz). This derivative was prepared and isolated independently by reaction of **9** with excess NaI in acetone.

(31) Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 209.

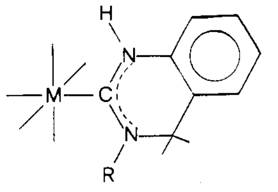
Scheme II



selective reactivity of the *o*-CH_2I group toward aromatic amines, undergoing nucleophilic substitution of the iodide (eq 1). Under these experimental conditions, the carbonyl and the isocyanide ligands are not attacked by the amine. The resulting products **14** and **15** can be looked at as novel organometallic functional isocyanides in which the dangling *o*-aminobenzyl function may potentially undergo further reactions. Thus, Dreiding molecular models indicate that the secondary amino goup in these derivatives might be in a favorable position to interact, at least in principle, with the coordinated isocyanide function to give intramolecularly cyclic amino–carbene species:



(1)



However, prolonged heating of **14** and **15** in *n*-heptane gave no evidence for the occurrence of such a reaction. This is in agreement with what was previously observed in the case of Cr and W complexes with hydroxyalkyl isocyanides, which only gave "open-chain" stable isocyanide derivatives with no tendency to cyclize via the free hydroxo function.[1] By contrast, cyclic carbenes are easily formed when such isocyanides are activated by coordination to metals such as Pd^{2+}, Pt^{2+}, Zn^{2+}, and Au^{3+}.[1] It appears therefore that the favorable special arrangement of the isocyanide and substituted amine functions in **14** and **15** is not backed up by sufficient activation of the isocyanide carbon toward nucleophilic attack, as is also reflected by the low value of $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$[27] (ca. 10 cm^{-1}, Table I). The inertness of the $-N{\equiv}C$ group toward nucleophiles is also borne out by the selectivity of the reactions of precursors **3** and **4** with aromatic amines.

The iodomethyl function in mononuclear complexes **3** and **4** displays the typical reactivity toward metal carbonyl anions that leads to novel M–C σ bonds. Since the *o*-CH_2I group is linked to an already metal-coordinated isocyanide moiety, either homo- or heterobinuclear derivatives are obtained, depending on the metal anion employed (Scheme IV).

Complexes **3** and **4** react with anions of the type $M'Cp(CO)_3^-$ (M = Mo, W; Cp = η^5-C_5H_5) in DME to form the corresponding σ-benzyl complexes **16**–**18** with 50–80% yield. The reaction of **4** with $Mn(CO)_5^-$ in THF affords complex **19** with 22% yield.

The IR spectra of **16**–**19** in the terminal CO stretching region match closely those reported for similar carbonyl configurations.[32-35] In the ^1H NMR spectra, the methylene proton signal is markedly shifted upfield upon formation of the new metal–benzyl σ bond. The observed values (Table II) agree with those previously reported for benzyl groups linked to transition metals.[32-35] In the homobinuclear complex **18** the CH_2 protons are coupled with ^{183}W ($I = {}^1/_2$, 14% natural abundance; $^2J(H-W) = 3.4$ Hz). The presence of two metal–carbonyl systems in quite distinct chemical environments in binuclear complexes **16**–**18** is clearly shown by the carbonyl ^{13}C NMR spectra (Table III). The "piano stool" geometry of the $M'Cp(CO)_3R$ group [R = *o*-$CH_2C_6H_4NCM(CO)_5$] in complexes **16**–**18** gives rise to two carbonyl resonances, one assigned to the CO trans to CH_2 (downfield) and the other to the CO's cis to CH_2 (upfield) in the spectral range 218–238 ppm, which is normal for compounds of this type containing an alkyl group.[36] The carbonyl resonances of the $M(CO)_5$ group do not differ significantly from those found in the mononuclear compounds $M(CO)_5(CN\frown CH_2X)$. In the case of the $Mn(CO)_5$ group (**19**) the carbonyl signal is broadened by ^{55}Mn ($I = {}^5/_2$, 100% natural abundance) as observed also for $Mn(CO)_5CH_2Ph$.[37] The methylene carbon chemical shifts

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(32) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709.

(33) Klein, B.; Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 1338.

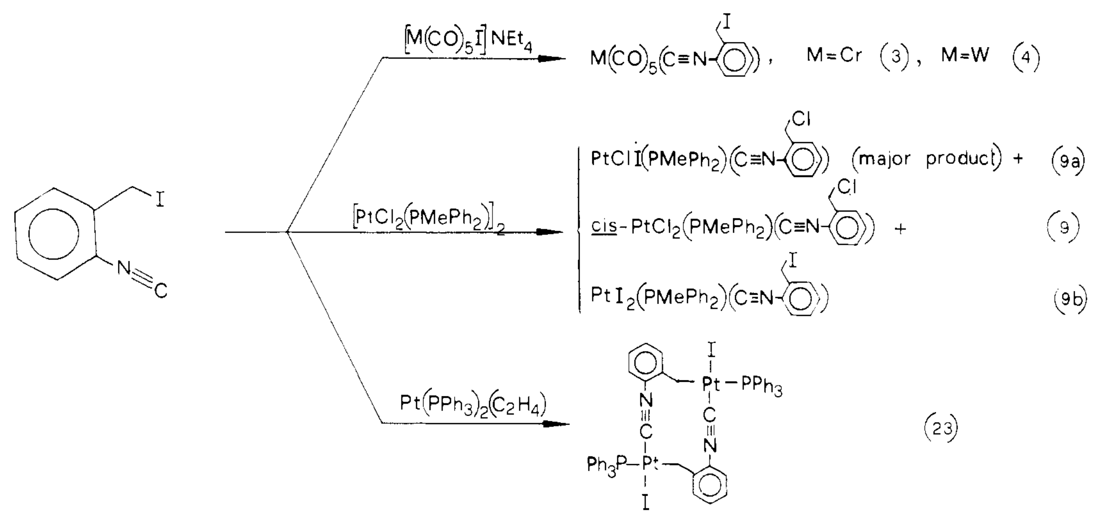
(34) Drew, D.; Darensbourg, M. Y.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73.

(35) Boschi, T.; Campesan, G.; Ros, R.; Roulet, R. *J. Organomet. Chem.* **1977**, *136*, 39.

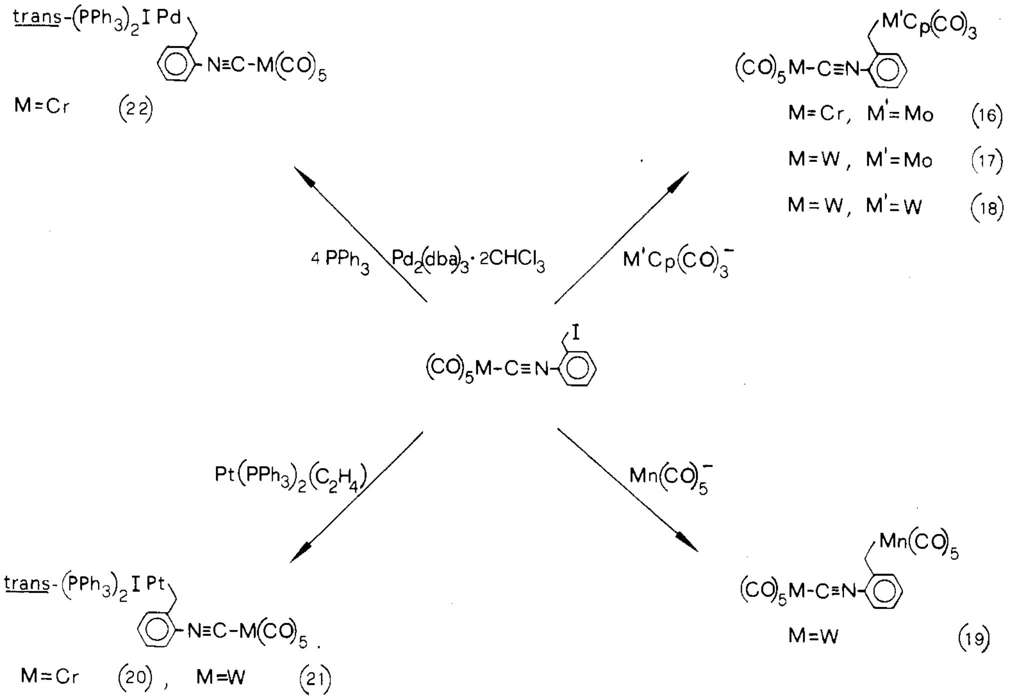
(36) Mann, B. E.; Taylor, B. F. in "^{13}C NMR Data for Organometallic Compounds"; Academic Press: London, 1981.

(37) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31.

Scheme III

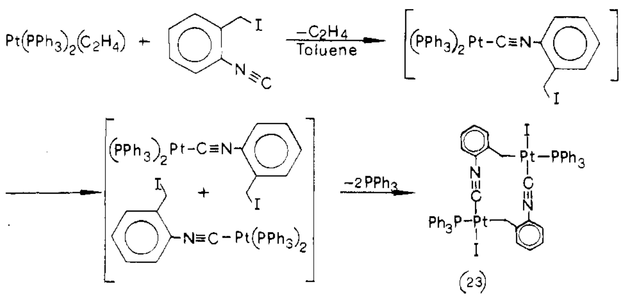


Scheme IV



are in the range +4 to −15 ppm, with an upfield shift going from Mn through Mo to W. Other typical $^{13}CH_2$ resonances are as follows: $[W(CO)_5CH_2Ph]^-$, δ 4.7;[38] $Mn(CO)_5CH_2Ph$, δ 8.7;[37] $MoCp(CO)_3CH_2Me$, δ −3.9;[40] $WCp(CO)_3Me$, δ −35.1;[39] $WCp(CO)_3CH_2CH{=}CH_2$, δ −6.6.[41] The chemical shift of the phenyl carbon directly bound to the methylene group undergoes a marked upfield shift (ca. 10 ppm) upon coordination of the α-CH_2 to the transition metal in compounds **16–19** (see first column under the heading "C_6H_4" in Table III). A similar shift has been reported for this phenyl carbon in the benzyl complex $Mn(CO)_5CH_2Ph$ (δ 151.0 vs. δ 137.3 for benzyl chloride).[37] Consistent with the above described formulations, the mass spectra of the binuclear complexes **16–19** showed the M^+ parent ion corresponding to the molecular weight of the complex, the identification of which was supported also by "fingerprint" mass spectral simulation.

Scheme V



Heterobinuclear complexes have been also prepared by oxidative addition of the o-CH_2I moiety in compounds **3** and **4** to low-valent Pd and Pt complexes with formation of new σ bonds (Scheme IV, complexes **20–22**). The trans square-planar geometry of the $PtI(PPh_3)_2CH_2$ moiety in **20** and **21** is clearly indicated by ^1H and ^{31}P NMR data (Table II). The methylene resonance is split into a triplet (1:2:1) by two

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(38) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

(39) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

(40) Braun, S.; Dahler, P.; Eilbracht, P. *J. Organomet. Chem.* **1968**, *146*, 135.

(41) Köhler, F. H.; Kalder, H. T.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *85*, C19.

equivalent phosphorus atoms with satellites due to coupling with ^{195}Pt, and the single ^{31}P resonance is also split into a triplet (1:4:1) by ^{195}Pt. The trans arrangement of the Pd fragment in complex **22** is suggested by the methylene signal multiplicity (triplet by coupling with phosphorus nuclei) in the ^{1}H NMR spectrum and by the presence of the phosphorus singlet in the ^{31}P spectrum.

It is noteworthy that the ability to undergo oxidative addition is featured also by the free functionalized isocyanide *o*-$ICH_2C_6H_4NC$ that reacts with $Pt(PPh_3)_2(C_2H_4)$ in toluene to give complex **23** (Scheme V). This reaction may involve, in principle, displacement of ethylene by isocyanide, oxidative addition, and PPh_3 elimination.

The intermediate Pt(0)-isocyanide species $Pt(PPh_3)_2(CN\frown CH_2I)$ could not be isolated; however, mixed isocyanide-phosphine Pt(0) derivatives have been previously described[42] and shown to undergo oxidative addition with alkyl halides to yield Pt(II) species.

Complex **23** has been characterized by elemental analysis, molecular weight measurement, and IR and NMR spectroscopy. The IR spectrum shows a strong $\nu(N{\equiv}C)$ band at 2170 cm^{-1}, which is typical for a Pt(II)-coordinated isocyanide (cf. complexes **8**–**10**). The *trans*-CH_2PtPPh_3 arrangement is deduced by the presence of a singlet (flanked by ^{195}Pt satellites) in the ^{31}P NMR spectrum, with a very low ^1J(P–Pt) value, as expected for a phosphine ligand trans to a σ-alkyl group.[43] Consistently, the ^3J(H–P) value of 10.4 Hz in the ^{1}H NMR spectrum falls in the range usually observed for Pt(II) complexes with mutually trans alkyl and phosphine ligands.[11e]

Conclusion

The functionalized isocyanides described in this paper did show the reactivity peculiar to each function. The coordinating ability of the isocyanide function afforded mononuclear complexes of Cr(0), W(0), Pd(II), and Pt(II). In some of these derivatives the free CH_2X function has been exploited to prepare other mononuclear complexes as well as new homo- and heterobinuclear species involving new M–C σ bonds. In such a way it was possible to hold in the same complex two metal centers even with very different electronic configurations and/or chemical environments. Such binuclear complexes are susceptible to further studies on possible cooperative effects between the two central metals in reactions involving the two functional groups such as the insertion of the isocyanide across the M–C σ bond. We are carrying out studies on the replacement of the halide in the CH_2X function with other functional substituents such as OH, NHR, SH, etc. with the aim of effecting intramolecular attack at the coordinated isocyanide leading to novel cyclic carbene complexes.

Acknowledgment. We thank Prof. B. Corain of the University of Padua for providing the mass spectra.

Registry No. **1**, 88656-97-7; **2**, 88656-98-8; **3**, 88656-99-9; **4**, 88657-00-5; **5**, 88728-22-7; **6**, 88728-82-9; **7**, 88728-23-8; **8**, 88657-01-6; **9**, 88657-02-7; **10**, 88657-03-8; **11**, 88657-04-9; **12**, 88657-05-0; **13**, 88657-06-1; **14**, 88657-07-2; **15**, 88657-08-3; **16**, 88657-09-4; **17**, 88657-10-7; **18**, 88657-11-8; **19**, 88657-12-9; **20**, 88657-13-0; **21**, 88657-14-1; **22**, 88657-15-2; **23**, 88657-16-3; $CN\frown CH_2Cl$, 88644-59-1; $CN\frown CH_2Cl$, 88644-60-4; $[Cr(CO)_5I][NEt_4]$, 14780-98-4; $[W(CO)_5I][NEt_4]$, 14781-01-2; $[Pd(PMePh_2)Cl_2]_2$, 29887-90-9; $PdCl_2(MeCN)_2$, 13869-38-0; (COD)$PtCl_2$, 12080-32-9; *trans*-$PtHCl(PPh_3)_2$, 16841-99-9; $MoCp(CO)_3^-$, 12126-18-0; $WCp(CO)_3^-$, 12126-17-9; $Mn_2(CO)_{10}$, 10170-69-1; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $Pd_2(dba)_3$, 51364-51-3; 2-(chloromethyl)benzoyl azide, 88644-61-5; 2-(chloromethyl)benzoyl chloride, 42908-86-1; 2-(chloromethyl)phenyl isocyanate, 52986-66-0; (2-(chloromethyl)phenyl)formamide, 88644-62-6.

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