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Bis(isothiocyanato)bis(phosphine) complexes of group 10 metals: reactivity toward organic isocyanides†

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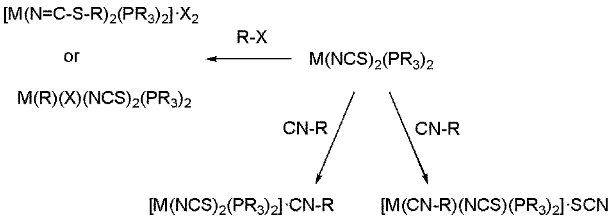
Treatment of $Ni(NCS)_2(PMe_2Ph)_2$ with organic isocyanides CN–R gave five-coordinate isocyanide Ni(II) complexes, $Ni(CN–R)(NCS)_2(PMe_2Ph)_2$ (R = C_6H_3-2,6-Me_2 (**1**), *t*-Bu (**2**)). Interestingly, the corresponding reaction of $Ni(NCS)_2(P(n\text{-}Pr)_3)_2$ with 2 equiv. of CN-*t*-Bu gave an unusual compound, which exists as an ion pair of the trigonal bipyramidal cation $[Ni(P(n\text{-}Pr)_3)_2(CN\text{-}t\text{-}Bu)_3]^{2+}$ (**3**) and the dinuclear NCS-bridged anion $[Ni(1,3\text{-}\mu\text{-}NCS)(NCS)_3]_2^{2-}$ (**4**). In contrast, $Pd(NCS)_2(P(n\text{-}Pr)_3)_2$ underwent substitution with 2 equiv. of CN-*t*-Bu to give the four-coordinate mono(isocyanide) Pd(II) complex $Pd(NCS)(SCN)(CN\text{-}t\text{-}Bu)(P(n\text{-}Pr)_3)$ (**5**) *via* phosphine dissociation. Reactions of $M(NCS)_2L_2$ (M = Pd, Pt; L = PMe_3, PEt_3, $PMePh_2$, $P(n\text{-}Pr)_3$) with two equiv. of CN–R (R = *t*-Bu, *i*-Pr, C_6H_3-2,6-Me_2) gave the corresponding bis(isocyanide) complexes $[M(CN–R)_2(PR_3)_2](SCN)_2$ (**7–13**), except for $Pd(NCS)_2(PEt_3)_2$ that reacted with CN–R′ (R′ = *i*-Pr, C_6H_3-2,6-Me_2) and produced the mono(isocyanide) Pd(II) complexes $[Pd(CN–R')(SCN)(PEt_3)_2](SCN)$ (**14** and **15**). Finally, treatment of $M(NCS)_2(PMe_3)_2$ (M = Ni, Pd, Pt) with sterically bulky isocyanide CN–C_6H_3-2,6-*i*-Pr_2 gave various products, (**16–18**) depending on the identity of the metal.

Introduction

The isothiocyanato (or thiocyanato) ligand in late transition-metal complexes, which belongs to pseudo-halide ligands such as azide (N_3) or isocyanate (NCO), has long been an interesting subject due to its various coordination modes: S- or N-coordination or bridging coordination through both S and N atoms.[1–3] Most of the isothiocyanato (or thiocyanato) complexes of late transition metals are typically prepared from metal halides and alkali metal isothiocyanates such as KSCN and NaSCN by metathesis in alcohol or aqueous media. Unfortunately, these reactions frequently give unwanted linkage isomers. For example, treating bis(dihalo)bis(phosphine or amine) metal complexes ($MX_2(PR_3)_2$ or $MX_2(NR_3)_2$) with KSCN or NaSCN gives various isomers such as $M(NCS)_2L_2$, $M(SCN)_2L_2$, and $M(NCS)(SCN)L_2$.[4–16] Recently, we have reported the preparation of isothiocyanato complexes of group 10 metals from bis(azido)bis(phosphine) complexes $[M(N_3)_2(PR_3)_2]$ (M = Ni, Pd, Pt) and $(CH_3)_3Si–NCS$ by replacing the N_3 ligands with the NCS group.[17]

Although many studies of the formation of late transition-metal isothiocyanato complexes and their coordination behaviour including linkage isomerization have been reported, studies of their reactivity toward electrophiles or nucleophiles are relatively rare.[18,19] In particular, chemical reactivity toward small molecules such as isocyanides has not been reported yet. Recently, we reported the formation of the adduct $[Ni(NCS)_2(PMe_3)_2]\cdot(CN\text{-}t\text{-}Bu)_2$ from the reaction of the bis(isothiocyanato) nickel complex $[Ni(NCS)_2(PMe_3)_2]$ with CN-*t*-Bu.[17] Unfortunately, we failed to determine the structure of this adduct due to its poor crystal quality. These results led us to decide to systematically investigate the reactivity of the isothiocyanato complexes of a nickel triad (group 10 metals) toward various organic isocyanides, which might form several possible products by adduct formation or substitution (Scheme 1). In addition, we tried to examine their reactivity toward organic halides (RX), which might lead to the formation of (1) metal–NCSR complexes by electrophilic attack of the halide at the NCS sulfur atom or (2) metal alkyls by oxidative-addition of the alkyl halides. We herein report the reactivity of bis(isothiocyanato)bis(phosphine) complexes of group 10 metals toward organic isocyanides and alkyl halides.



Scheme 1

Results and discussion

Reactions of bis(isothiocyanato) Ni(II) complexes with isocyanides

In this work, all starting materials $M(NCS)_2L_2$ (M = Ni, Pd, Pt; L = tertiary or chelating phosphines) were obtained from the reaction of bis(azido) metal complexes $M(N_3)_2L_2$ with $Me_3Si–NCS$ using our previous methods.[17] In preparing bis(isothiocyanato) complexes, compared with the conventional metathesis using KSCN (or NaSCN), these methods appear to have the advantage of suppressing the formation of linkage isomers.

Treating the bis(isothiocyanato) Ni(II) complex $Ni(NCS)_2L_2$ with 2 equiv. of isocyanides (CN–C_6H_3-2,6-Me_2 and CN-*t*-Bu)

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† Electronic supplementary information (ESI) available: NMR data for all complexes. See http://dx.doi.org/10.1039/b508134c

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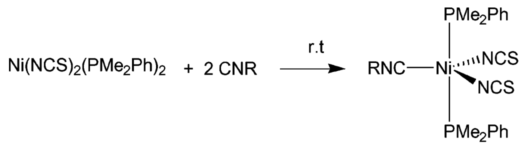
gave the mono(isocyanide) Ni(II) complexes, $Ni(NCS)_2(CN{-}R)L_2$, as shown in eqn (1)



$$Ni(NCS)_2(PMe_2Ph)_2 + 2\,CNR \xrightarrow{r.t} RNC{-}Ni(NCS)_2(PMe_2Ph)_2$$

(R = C_6H_3-2,6-Me_2, **1**; *t*-Bu, **2**) (1)

These reactions proceed smoothly at room temperature. Complexes **1** and **2** were isolated as brown crystals and characterized by spectroscopy and elemental analysis (see the supporting information and Table 1). The molecular structure of **1** was determined by X-ray diffraction. IR spectra of the complexes show a sharp absorption band at 2135 (for **1**) and 2186 cm^{-1} (for **2**) due to the C≡N group of the isocyanide ligand and one broad band at 2072 cm^{-1} (for **1**) and two sharp bands at 2093 and 2078 cm^{-1} (for **2**), whereas those of the starting material display a single absorption band at 2091 cm^{-1} corresponding to the terminal NCS ligands. $^{13}C\{^1H\}$ NMR spectra display a signal at *ca.* 130 ppm corresponding to the NCS carbon atom, but the CN–R carbon atom signals are not observed, probably because of their too weak intensities. A singlet in the $^{31}P\{^1H\}$ NMR spectra of both complexes strongly supports the formation of a single product $Ni(NCS)_2(CN{-}R)(PMe_2Ph)_2$, indicating the absence of linkage isomers at least in solution. Unexpectedly, proposed neutral TBP Ni complexes (**1**, **2** and **18**) indicate somewhat molar conductance in methanol solution, which are less than those data of the ionic Pd(II) or Pt(II) complexes as shown in Table 1. Considering these conductivities, the formation of ionic square planar complexes, $[Ni(R{-}NC)(NCS)(PMe_2Ph)](SCN)$, or partial ionization in solution may occur.

The ORTEP drawing of compound **1** with the atom-numbering scheme is shown in Fig. 1. Crystallographic data and bonding parameters are given in Table 2. The coordination sphere of Ni can be described as a trigonal bipyramid (TBP), with two isothiocyanato ligands and one 2,6-dimethylphenyl

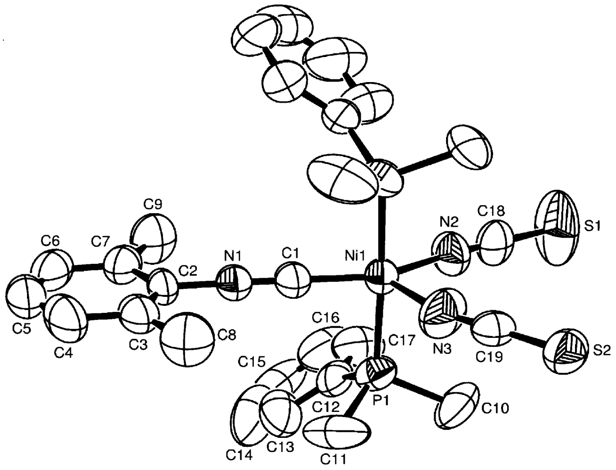


Fig. 1 ORTEP drawing[66] of **1** showing the atom-labelling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ni1–C1 1.773(9), Ni1–N2 1.899(9), Ni1–N3 2.097(9), Ni1–P1 2.2084(18), S1–C18 1.608(12), S2–C19 1.605(11), N1–C1 1.163(9), N1–C2 1.405(10), N2–C18 1.130(11), N3–C19 1.142(11); C1–Ni1–N2 147.3(4), C1–Ni1–N3 114.6(4), N2–Ni1–N3 98.0(4), C1–Ni1–P1 88.38(6), N2–Ni1–P1 92.23(7), N3–Ni1–P1 89.21(7), C1–N1–C2 178.8(10), C18–N2–Ni1 172.8(9), C19–N3–Ni1 158.8(10).

Table 1 Colors, yields, analytical data and molar conductances

Complex	Color	Yield (%)	Analyses[b] C (%)	H (%)	N (%)	Molar conductance[c]
1, $Ni(NCS)_2(CN{-}R)(PMe_2Ph)_2$ (R = C_6H_3-2,6-Me_2)	Brown	90	55.99 (55.69)	5.45 (5.37)	7.20 (7.22)	56
2, $Ni(NCS)_2$(CN-*t*-Bu)$(PMe_2Ph)_2$	Brown	85	52.04 (51.70)	6.11 (5.85)	7.92 (7.86)	59
3·4 [Ni(P(*n*-Pr)$_3$)$_2$(CN-*t*-Bu)$_3$]·[Ni(1,3-μ-NCS)$(NCS)_3$]$_2$	Yellow	30	45.72 (45.44)	7.15 (7.12)	9.80 (9.76)	106
5, Pd(NCS)(SCN)(CN-*t*-Bu)(P(*n*-Pr)$_3$)	Yellow	95	41.59 (41.24)	6.67 (6.49)	8.92 (9.02)	4
7, [Pd(CN-*t*-Bu)$_2$$(PMe_3)_2$]$(SCN)_2$	Yellow	94	40.31 (39.96)	6.83 (6.71)	10.32 (10.36)	90
8, [Pd(CN-*t*-Bu)$_2$$(PMePh_2)_2$]$(SCN)_2$	Yellow	88	57.61 (57.83)	5.69 (5.62)	6.84 (7.10)	80
9, [Pd(CN-*i*-Pr)$_2$$(PMe_3)_2$]$(SCN)_2$	Yellow	68	37.34 (37.46)	6.58 (6.29)	10.87 (10.92)	113
10, $[Pd(CN{-}R)_2(PMePh_2)_2](SCN)_2$ (R = C_6H_3-2,6-Me_2)	Yellow	82	62.54 (62.40)	5.22 (5.01)	6.26 (6.33)	85
11, $[Pt(CN{-}R)_2(PMe_3)_2](SCN)_2$ (R = C_6H_3-2,6-Me_2)	Yellow	68	42.93 (43.03)	5.04 (5.00)	7.70 (7.72)	114
12, $[Pt(CN{-}R)_2(PEt_3)_2](SCN)_2$ (R = C_6H_3-2,6-Me_2)	White	52	47.02 (47.46)	6.07 (5.97)	6.77 (6.92)	98
13, $[Pt(CN{-}R)_2$(P(*n*-Pr)$_3$)$_2$]$(SCN)_2$ (R = C_6H_3-2,6-Me_2)	Yellow	89	51.31 (51.05)	6.99 (6.76)	6.34 (6.27)	95
14, $[Pd(CN{-}R)(SCN)(PEt_3)_2](SCN)$ (R = *i*-Pr)	Yellow	90	41.39 (40.95)	7.09 (7.06)	7.86 (7.96)	85
15, $[Pd(CN{-}R)(SCN)(PEt_3)_2](SCN)$ (R = C_6H_3-2,6-Me_2)	Yellow	80	47.04 (46.82)	6.81 (6.66)	6.97 (7.12)	84
16, $[Pd(CN{-}Ar)_2(PMe_3)_2](SCN)_2$ (Ar = C_6H_3-2,6-*i*-Pr_2)	Orange	79	54.24 (54.50)	7.20 (6.99)	7.24 (7.48)	84
17, $[Pt(CN{-}Ar)_2(PMe_3)_2](SCN)_2$ (Ar = C_6H_3-2,6-*i*-Pr_2)	Yellow	56	49.13 (48.73)	6.49 (6.25)	6.50 (6.69)	89
18, $Ni(CN{-}Ar)(NCS)_2(PMe_3)_2$ (Ar = C_6H_3-2,6-*i*-Pr_2)	Brown	91	49.35 (49.04)	7.07 (6.86)	8.31 (8.17)	36
19[a], $[Pt(depe)_2](SCN)_2$	White	72	36.13 (36.51)	6.91 (6.68)	3.76 (3.87)	181

[a] depe = 1,2-bis(diethylphosphino)ethane. [b] Calculated values are given in parentheses. [c] In MeOH solution at 25 °C, 10^{-3} M. Units: $\Omega^{-1}cm^2\,mol^{-1}$.

Table 2 X-Ray data collection and structure refinements

	1	**3·4**·CH_2Cl_2	**5**	$Pd(NCS)_2L_2$	**8**	**11**	**12**	**19**
Formula	$C_{27}H_{31}N_3NiP_2S_2$	$C_{38}H_{71}Cl_2N_7Ni_2P_2S_4$	$C_{16}H_{30}N_3PPdS_2$	$C_{20}H_{42}N_2P_2PdS_2$	$C_{38}H_{44}N_4P_2PdS_2$	$C_{26}H_{36}N_4P_2PtS_2$	$C_{32}H_{48}N_4P_2PtS_2$	$C_{22}H_{48}N_2P_4PtS_2$
FW	582.32	1004.52	465.92	543.02	789.23	725.74	809.89	723.71
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal size/mm^3	0.18 × 0.16 × 0.14	0.20 × 0.18 × 0.16	0.44 × 0.40 × 0.20	0.20 × 0.18 × 0.16	0.44 × 0.40 × 0.30	0.32 × 0.26 × 0.24	0.28 × 0.22 × 0.16	0.50 × 0.30 × 0.16
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$Pnma$	$P\bar{1}$	$Pca2_1$	$P\bar{1}$	$P2_1$	Pn	$P\bar{1}$	$P\bar{1}$
a/Å	14.503(3)	13.104(4)	13.5684(12)	8.7268(9)	10.029(4)	8.1931(9)	9.9813(15)	11.103(3)
b/Å	12.9769(15)	13.141(4)	9.0189(5)	9.3401(12)	11.899(3)	12.2373(18)	12.1211(14)	11.378(4)
c/Å	15.918(3)	17.539(3)	18.6982(14)	17.114(2)	17.761(5)	15.4579(17)	16.122(3)	12.928(3)
α/°	—	81.16(2)	—	89.676(9)	—	—	90.367(12)	101.485(17)
β/°	—	82.24(2)	—	86.225(9)	103.217(16)	97.128(9)	104.795(12)	90.380(17)
γ/°	—	67.39(2)	—	87.750(10)	—	—	104.703(11)	91.10(2)
V/Å^3	2995.9(9)	2746(1)	2288.1(3)	1390.9(3)	2063(1)	1537.9(3)	1818.7(5)	1600.0(8)
Z	4	2	4	2	2	2	2	2
D_c/g cm^{-3}	1.291	1.215	1.353	1.297	1.270	1.567	1.479	1.502
μ, mm^{-1}	0.914	1.024	1.066	0.940	0.658	4.823	4.086	4.728
$F(000)$	1216	1064	960	568	816	720	816	728
T_{min}	0.5501	0.3056	0.2285	0.6359	0.6940	0.3811	0.4418	0.2221
T_{max}	0.5935	0.7435	0.2961	0.8930	0.8993	0.7857	0.8153	0.6865
No. of reflns measured	2731	10037	2079	5192	4019	2900	6740	5833
No. of reflns unique	2731	9585	2079	4843	3795	2900	6345	5525
No. of reflns with $I > 2\sigma(I)$	1188	4834	1956	3783	3569	2646	5452	4528
No. of params refined	184	481	209	247	424	320	344	269
Max., min, peak, hole/e Å^{-3}	0.535, −0.429	0.915, −0.709	0.335, −0.575	0.413, −0.446	0.531, −0.279	0.658, −0.642	1.421, −0.740	1.741, −1.085
GOF on F^2	1.000	1.031	1.061	1.050	1.058	1.081	1.055	1.080
R	0.0661	0.0940	0.0281	0.0343	0.0310	0.0319	0.0407	0.0377
$wR_2{}^a$	0.1170	0.2354	0.0723	0.0816	0.0783	0.0785	0.0987	0.0986
R (all data)	0.1722	0.1797	0.0305	0.0496	0.0346	0.0379	0.0514	0.0466
$wR_2{}^a$ (all data)	0.1542	0.2974	0.0741	0.0894	0.0812	0.0823	0.1053	0.1069

[a] $wR_2 = ([w(F_o{}^2 - F_c{}^2)^2]/([w(F_o{}^2)^2]^{1/2}$

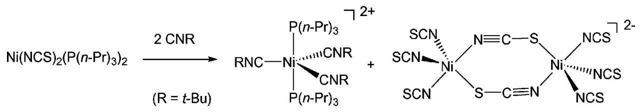
isocyanide ligand at equatorial sites. All isothiocyanate atoms, cyanide atoms, and the nickel atom lie on the crystallographic mirror plane, which is coincident with the molecular plane.

Strangely, one isothiocyanato ligand (N3–C19–S2) is coordinated to the Ni atom in a strongly bent manner with the Ni–N–C bond angle of 158.8(10)°. Two absorption bands for complex **2** may arise from this bent Ni–NCS and the other linear Ni–NCS linkage. The Ni–C (CNR) bond length (1.773(9) Å) is close to that (1.787(3) Å) of [Ni(triphos)(CN-xylyl)], but it is shorter than those (1.81–1.92 Å) found for other isocyanide Ni complexes,[20–29] indicating a somewhat strong coordination of CN–R to the Ni center.

Earlier works by Ibers and co-workers suggested the TBP Ni(II) complex Ni(CN)$_2$(PMe$_2$Ph)$_3$ to have two cyano ligands at axial sites and three phosphine ligands at equatorial sites.[30] However, as shown in Fig. 1, complex **1** has a distorted TBP geometry with two phosphine ligands at axial sites and one cyano and two isothiocyanato (NCS) ligands at equatorial sites. This ligand arrangement in complex **1** probably arises from the sterically demanding 2,6-dimethylphenyl isocyanide ligand that prefers to occupy the sterically less hindered equatorial sites.

The formation of five-coordinate TBP Ni(II) complexes containing an isocyanide group has been proposed by several research groups.[23,26,31] Although several isocyanide Ni complexes have been reported, trigonal bipyramidal Ni-isocyanide complexes have never been structurally characterized by X-ray diffraction. Moreover, those Ni complexes have been frequently proposed as intermediates or precursors in catalytic processes of isocyanide polymerization and olefin polymerization.[24,26,31]

Interestingly, treating Ni(NCS)$_2$[P(n-Pr)$_3$]$_2$ with two equiv. of t-Bu isocyanide gave an unusual compound, which exists as an ion pair of the trigonal bipyramidal cation [Ni(P(n-Pr)$_3$)$_2$(CN-t-Bu)$_3$]$^{2+}$ (**3**) and the dinuclear NCS-bridged anion [Ni(1,3-μ-NCS)(NCS)$_3$]$_2^{2-}$ (**4**) (eqn (2)). The formulation of this ion pair was determined on the basis of conductivity, magnetic moment, and NMR data of the compound. The conductivity value (106 Λ_M) for the mixture at 25 °C in methanol is close to those values (80–114 Λ_M) for the ionic Pd(II) or Pt(II) complexes (Table 1) and is definitely much higher than those of neutral TBP Ni(II) complexes **1** and **2**. This observation strongly indicates that the mixture exists as an ion pair rather than two independent neutral species. In addition, the effective magnetic moment (μ_{eff}) of the compound at room temperature is 2.71 μ_B, which is quite close to the spin-only value (2.83 μ_B) for two unpaired electrons and is consistent with a trigonal bipyramidal d^8 Ni(II) complex. Considering these conductivity and magnetic moment values together, every nickel in this compound attains an 18-electron configuration, regardless of different oxidation states (+2 in the dicationic species **3** and +3 in the dianionic species **4**).



(2)

The IR spectrum of the compound shows a sharp band at 2168 cm^{-1} due to the C≡N group of CN–R and one strong band at 2074 cm^{-1} due to the terminal and bridging NCS groups. The molecular structure of the compound clearly demonstrated the existence of two different molecules. Fig. 2A shows a PLUTO drawing of compound **3** that has a typical TBP structure, and Fig. 2B shows an ORTEP drawing of compound **4** that has a dinuclear structure with pseudo-TBP nickel(III) centers bridged by the NCS ligands. The reason why we presented the PLUTO drawing for compound **3** is the extreme difficultly in labelling carbon atoms in the t-Bu groups. As shown in Fig. 2A, three isocyanides (CN-t-Bu) form an equatorial plane of the TBP geometry of a dicationic species **3**. The Ni–C bond lengths (1.868(10)–1.879(9) Å) of **3** are within the range of values found for other isocyanide Ni(II) complexes.[23–29] The dianion **4** (Fig. 2B) is a unique dinuclear Ni(III)-isothiocyanate species with no supporting ligands. The Ni–N bond lengths (1.98–2.03 Å) are close to those (1.90–2.10 Å) found for other dinuclear Ni(II) complexes containing bridging NCS ligands,[32–39] and therefore bond lengths do not seem to be a clear criterion for the assignment of the oxidation state of the Ni metals in the mixture of **3** and **4**. Most dinuclear Ni(II) complexes having bridging NCS ligands contain octahedral or distorted octahedral Ni moieties, but examples of dinuclear pseudo-TBP Ni complexes with bridging NCS ligands are rare and unusual.

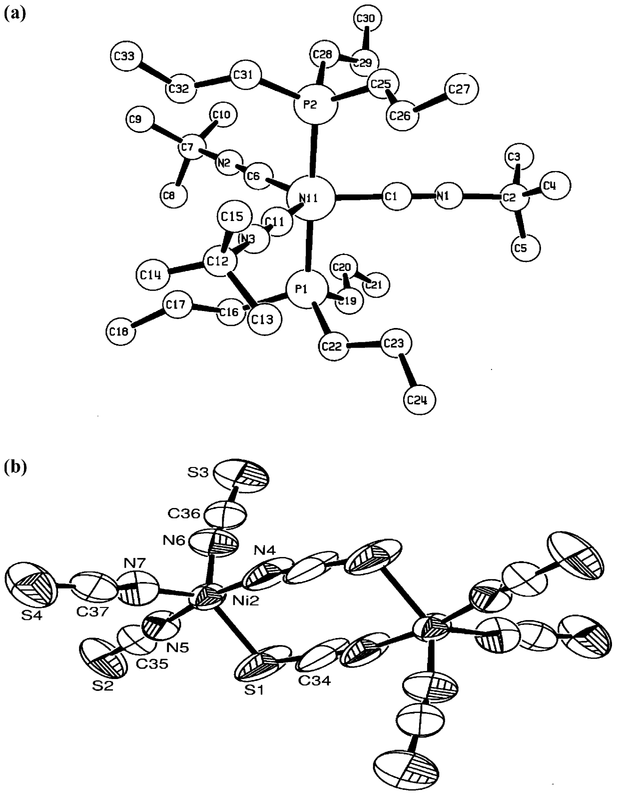
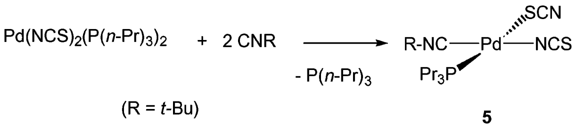


Fig. 2 ORTEP drawing[66] of (**3**)·(**4**)·CH$_2$Cl$_2$: Fig. 2A, [Ni(P(n-Pr)$_3$)$_2$(CN-t-Bu)$_3$]$^{2+}$; Fig. 2B, [Ni(1,3-μ-NCS)(NCS)$_3$]$_2^{2-}$. Selected bond lengths (Å) and angles (°): Ni1–C1 1.868(10), Ni1–C11 1.870(9), Ni1–C6 1.879(9), Ni1–P2 2.227(2), Ni1–P1 2.239(2) Ni2–N7 1.980(10), Ni2–N6 1.984(11), Ni2–N5 1.997(9), Ni2–N4 2.025(10), N2–S1 2.414(3); C1–Ni1–C11 120.9(4), C1–Ni1–C6 119.1(4), C11–Ni1–C6 120.0(3), P2–Ni1–P1 179.7(11), N7–Ni2–N6 105.3(4), N7–Ni2–N5 93.9(4), N6–Ni2–N5 92.9(4), N7–Ni2–N4 93.8(5), N6–Ni2–N4 91.2(5), N5–Ni2–N4 170.0(4), N7–Ni2–S1 122.1(3), N5–Ni2–S1 83.2(3).

Numerous reports on the dinuclear or trinuclear Ni complexes having chelating amines or 1,3-bridging NCS groups have appeared.[32–47] In addition, the molecular structure of the dinuclear μ-NCS-bridged Pt-phosphine (P(n-Pr)$_3$) complex was previously reported.[48] To our best knowledge, complex **4** is the first example of a homoleptic and dinuclear Ni–NCS complex without any supporting ligands such as phosphines or amines.

Reactions of bis(isothiocyanato) Pd(II) and Pt(II) complexes with isocyanides

The bis(isothiocyanato)bis(phosphine) complex Pd(NCS)$_2$(P(n-Pr)$_3$)$_2$ reacted with 2 equiv. of CN-t-Bu to give the 4-coordinate mono(isocyanide) Pd(II) complex Pd(NCS)(SCN)(CN-t-Bu)(P(n-Pr)$_3$) (**5**) by the replacement of phosphine with CN-t-Bu (eqn (3)).



(3)

The IR spectrum of **5** shows a strong band at 2218 cm^{-1} due to the CN–R and two bands at 2096 and 2064 cm^{-1} assignable to the two terminal NCS or SCN groups. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the complex are consistent with the proposed formulation. The molecular structure of complex **5** gives concrete evidence for the formation of an isocyanide Pd(II) complex (Fig. 3). Fig. 3 clearly shows two distinct coordination modes (or a linkage isomerism) of the two NCS ligands, a N-bound NCS *trans* to the isocyanide and a S-bound NCS *trans* to the phosphine. On the basis of the hard-soft acid–base concept, anti-symbiosis appears to work in complex **5** in which the hard atom (the NCS nitrogen) prefers to bind to the metal *trans* to the hard atom (the isocyanide carbon) and the soft atom (the NCS sulfur) *trans* to the soft atom (the phosphine phosphorus).

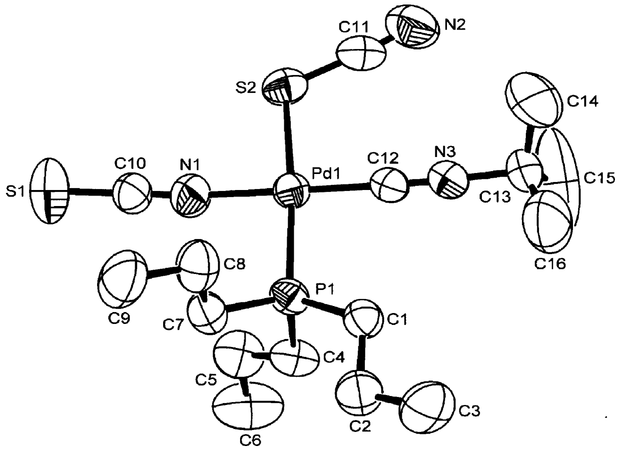


Fig. 3 ORTEP drawing[66] of **5**. Selected bond lengths (Å) and angles (°): Pd1–C12 1.917(6), Pd1–N1 1.995(6), Pd1–P1 2.2860(12), Pd1–S2 2.3824(14), S1–C10 1.607(6), S2–C11 1.656(8), N1–C10 1.138(9), N2–C11 1.148(9), N3–C12 1.143(9); C12–Pd1–N1 178.8(3), P1–Pd1–S2 175.28(6), C11–S2–Pd1 107.7(2), C10–N1–Pd1 167.7(6), N1–C10–S1 179.2(6), N2–C11–S2 175.7(6), N3–C12–Pd1 178.0(5).

The above result (eqn (3)) is quite different from the case for the nickel analogue (Ni(NCS)$_2$(P(n-Pr)$_3$)$_2$) (eqn (2)), which reacts with CN-t-Bu to give a TBP Ni(II) complex and a homoleptic isothiocyanato Ni(III) complex. In order to gain more insight into the linkage isomerization, we have characterized the starting material. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the starting material Pd(NCS)$_2$(P(n-Pr)$_3$)$_2$ revealed the presence of three linkage isomers of Pd(NCS)$_2$L$_2$, Pd(NCS)(SCN)L$_2$, and Pd(SCN)$_2$L$_2$ (in the ratio of 0.51 : 1.00 : 0.28 based on the integration ratio by ^{31}P{^{1}H} NMR). This phenomenon agrees with that found for ((PhCH$_2$)$_3$P)$_2$Pd(NCS)$_2$ prepared from a Pd(II) dichloride complex and KSCN.[5] By repeated recrystallizations of the starting material, X-ray quality crystals could be obtained. Interestingly, its molecular structure clearly exhibited two linkage isomers (Fig. 4): Pd(NCS)$_2$L$_2$ and Pd(SCN)$_2$L$_2$ (L = P(n-Pr)$_3$). The two independent Pd atoms in these isomers both lie on inversion centers. It should be mentioned that the corresponding Ni complex Ni(NCS)$_2$(P(n-Pr)$_3$)$_2$ does not show linkage isomerism both in the solid state and in solution.

Many studies of the linkage isomerization of thiocyanato phosphine Pd(II) complexes have been reported, which has been attributed to various factors such as electronic or steric factors of ligands and medium effects.[4–10] Particularly, Balch and co-workers showed the linkage isomerization for thiocyanato Pd(II) complexes having chelating phosphine ligands by spectroscopy and X-ray diffraction.[4] We believe that the formation of **5** *via* phosphine dissociation is probably a direct consequence of the presence of the linkage isomers in the starting material Pd(NCS)$_2$(P(n-Pr)$_3$)$_2$.

When Pd(NCS)$_2$(P(n-Pr)$_3$)$_2$ was treated with 2 equiv. of CN-i-Pr at room temperature, the ionic bis(isocyanide) Pd(II) complex {Pd[P(n-Pr)$_3$]$_2$(CN-i-Pr)$_2$}(NCS)$_2$ (**6**) was obtained and characterized by spectroscopy (IR, ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR). The conductivity (98 Λ_M at 25 °C in MeOH) supports complex **6** existing as an ionic compound in solution rather than the neutral adduct [Pd(NCS)$_2$(P(n-Pr)$_3$)$_2$]·2(CN-i-Pr). The IR spectrum of **6** shows a strong band at 2224 cm^{-1} due to the CN–R and two bands at 2096 and 2052 cm^{-1} due to the NCS or SCN groups. However, several recrystallizations of **6** in CH$_2$Cl$_2$/ether/hexane resulted in the loss of the isocyanide ligand (similar isocyanide dissociation was also observed, as shown in eqn (7)) and caused it to go back to the starting material.

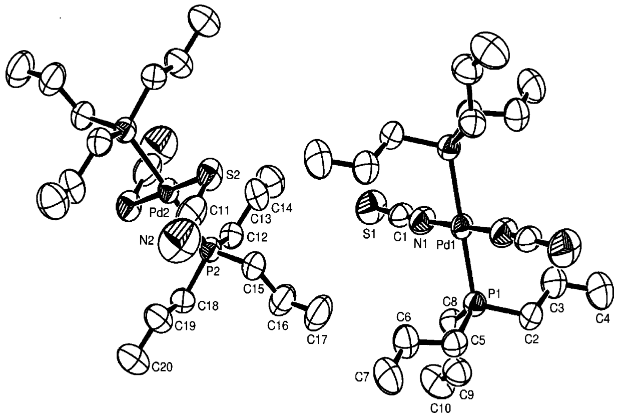
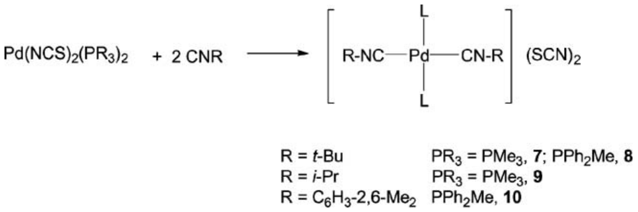


Fig. 4 ORTEP drawing[66] of Pd(NCS)$_2$L$_2$·Pd(SCN)$_2$L$_2$ (L = P(n-Pr)$_3$). Selected bond lengths (Å) and angles (°): Pd1–N1 1.983(3), S1–C1 1.612(4), N1–C1 1.130(5), Pd2–S2 2.3371(10), S2–C11 1.647(6), N2–C11 1.148(6); C1–N1–Pd1 176.5(3), N1–C1–S1 179.8(4), S2–Pd2–P2 92.93(4), C11–S2–Pd2 99.80(18), N2–C11–S2 176.7(6).

To further examine the effects of supporting ligands (phosphines) and attacking isocyanides, we have carried out the reactions of Pd(NCS)$_2$L$_2$ (L = PMe$_3$, PMePh$_2$) with 2 equiv. of CN–R (R = t-Bu, i-Pr, C$_6$H$_3$-2,6-Me$_2$) as shown in eqn (4).



(4)

These reactions gave a series of the ionic bis(isocyanide) Pd(II) complexes [Pd(CN–R)$_2$(PR$_3$)$_2$](SCN)$_2$ (**7–10**), in which the SCN groups lie outside the coordination sphere as counterions. The products were obtained as yellow solids in 80–94% yields. The IR spectra of the complexes display a strong band at 2190–2229 cm^{-1} due to the isocyanide ligand and another strong band at 2047–2070 cm^{-1} due to the SCN ions. The integration ratios in the ^{1}H NMR spectra of the complexes are consistent with the proposed structure. A singlet in the ^{31}P{^{1}H} NMR spectra of the complexes suggests a symmetric orientation of the ligands. The molecular structure of **8** clearly demonstrates the formation of the ionic bis(isocyanide) Pd(II) complex [Pd(CN-t-Bu)$_2$(PMePh$_2$)$_2$](SCN)$_2$, which shows a square planar geometry with *trans* isocyanides and *trans* phopshines, together with two SCN^{-} counterions (Fig. 5). Many isocyanide Pd(I) or Pd(II) complexes with halides (Cl, Br) or pseudo halides (PF$_6$, SbF$_6$, B(C$_6$H$_5$)$_4$, ClO$_4$, OAc, OTf) have been reported.[49–60] Some of them are unstable in the solid state or in solution at room temperature and often lose the isocyanide(s). Our Pd(II) complexes **7–10** (in eqn (4)) exhibit a relatively high stability both in the solid state and in solution. For instance, several repeated recrystallizations do not bring about the loss of the isocyanide ligand, indicating a relatively strong coordination of the isocyanide to the metal center.

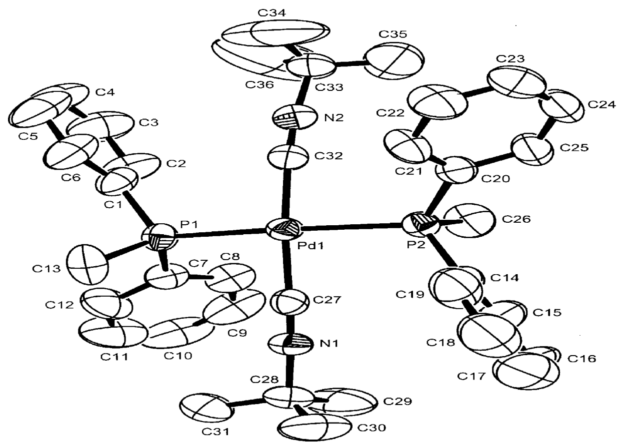
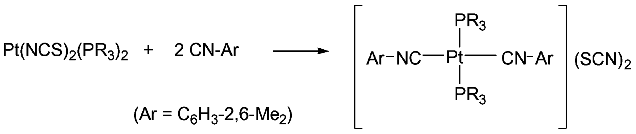


Fig. 5 ORTEP drawing [66] of **8**. Selected bond lengths (Å) and angles (°): Pd1–C27 1.987(5), Pd1–C32 1.987(5), Pd1–P1 2.3596(14), Pd1–P2 2.3590(14), S1–C37 1.544(12), S2–C38 1.657(9), N3–C37 1.063(18), N4–C38 1.154(10); C27–Pd1–C32 169.7(2), C27–Pd1–P1 86.67(14), C32–Pd1–P1 93.46(15), C27–Pd1–P2 90.69(14), C32–Pd1–P2 87.27(15), P1–Pd1–P2 169.12(5).

Consistent with our expectation, treatments of $Pt(NCS)_2(PR_3)_2$ (R = Me, Et, *n*-Pr) with 2 equiv. of CN–Ar (Ar = C_6H_3-2,6-Me_2) also gave the bis(isocyanide) Pt(II) complexes $[Pt(CN–Ar)_2(PR_3)_2](SCN)_2$ (**11–13**) in 52–89% yields (eqn (5)).



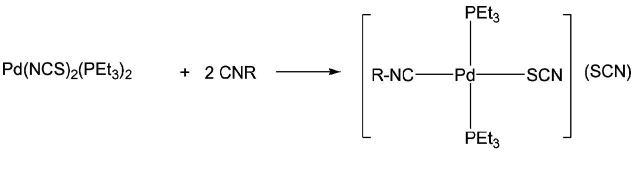
$$Pt(NCS)_2(PR_3)_2 + 2\ CN\text{-}Ar \longrightarrow \left[Ar\text{-}NC\text{—}\overset{PR_3}{\underset{PR_3}{Pt}}\text{—}CN\text{-}Ar \right](SCN)_2$$

(Ar = C_6H_3-2,6-Me_2)

R = Me, **11**
R = Et, **12**
R = n-Pr, **13**

(5)

The IR spectra of the complexes **11–13** show one C≡N stretching band at 2189–2194 cm^{-1} and one SCN stretching band at 2048–2052 cm^{-1}. Molecular structures of the cationic parts of **11** and **12** clearly show a square planar geometry, with *trans* phosphines and *trans* isocyanides as well as two SCN^- counterions (Figs. 6 and 7). This type of coordination was previously observed for the other Pt(II) complexes of $[Pt(CN–R)_2L_2]X_2$ (L = PR_3; X = BF_4, PF_6, Cl).[61–63] In contrast, the corresponding reactions of $Pd(NCS)_2(PEt_3)_2$ with 2 equiv. of CN–R produced totally different products, the ionic mono(isocyanide) Pd(II) complexes $[Pd(CN–R)(SCN)(PEt_3)_2](SCN)$ (R = *i*-Pr (**14**), C_6H_3-2,6-Me_2 (**15**)) (eqn (6)).



$$Pd(NCS)_2(PEt_3)_2 + 2\ CNR \longrightarrow \left[R\text{-}NC\text{—}\overset{PEt_3}{\underset{PEt_3}{Pd}}\text{—}SCN \right](SCN)$$

R = *i*-Pr, **14**
R = C_6H_3-2,6-Me_2, **15**

(6)

Complexes **14** and **15** were isolated as yellow solids and characterized by spectroscopy (IR, NMR), analytical data and conductivities. IR spectra of the complexes display one C≡N stretching band at 2249 (for **14**) or 2196 (for **15**) cm^{-1} and two strong SCN bands at 2114 and 2057 (for **14**) cm^{-1} or 2106 and 2056 (for **15**) cm^{-1}. The IR absorption bands of the S-bound and N-bound NCS ligands in Pd complexes are known to appear at 2130–2100 cm^{-1} and below 2100 cm^{-1}, respectively.[4] Although the poor crystal quality of the products prevented us from their structural characterization by X-ray diffraction, the conductivity data as shown in Table 1 support the formation of ionic four-coordinate square planar complexes.

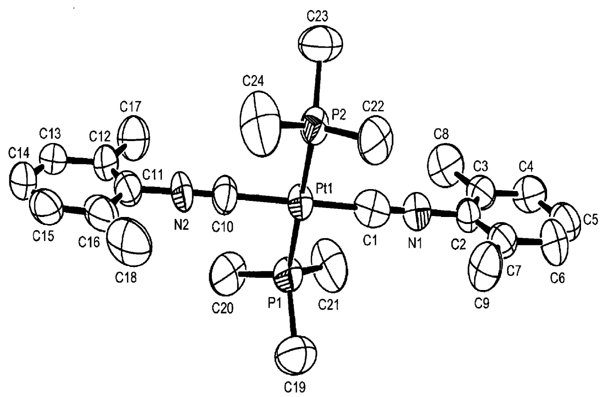


Fig. 6 ORTEP drawing [66] of **11**. Selected bond lengths (Å) and angles (°): Pt1–C1 1.899(15), Pt1–C10 1.997(12), Pt1–P1 2.345(3), Pt1–P2 2.316(3), S1–C25 1.56(2), S2–C26 1.70(3), N3–C25 1.14(3), N4–C26 1.06(3); C1–Pt1–C10 177.1(5), C1–Pt1–P1 89.8(3), C10–Pt1–P1 88.2(3), C1–Pt1–P2 90.5(3), C10–Pt1–P2 91.4(3), P1–Pt1–P2 176.21(11).

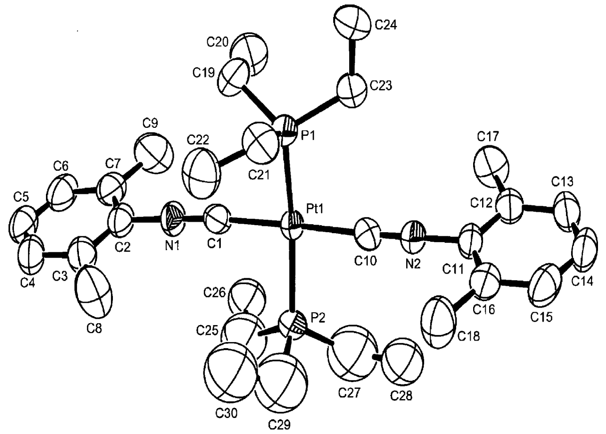
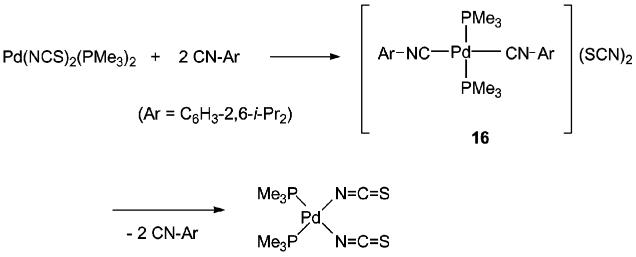


Fig. 7 ORTEP drawing [66] of **12**. Selected bond lengths (Å) and angles (°): Pt1–C1 1.927(7), Pt1–C10 1.955(7), Pt1–P1 2.3468(17), Pt1–P2 2.3575(18), S1–C31 1.646(12), N3–C31 1.130(13), S2–C32 1.677(18), N4–C32 0.880(19); C1–Pt1–C10 173.9(3), C1–Pt1–P1 90.4(2), C10–Pt1–P1 88.4(2), C1–Pt1–P2 88.4(2), C10–Pt1–P2 91.59(19), P1–Pt1–P2 167.99(7).

As shown in eqns (4)–(6), reactions of $M(NCS)_2(PR_3)_2$ (M = Pd or Pt) with 2 equiv. of isocyanide led to the formation of mono(isocyanide) or bis(isocyanide) metal complexes, depending on the supporting ligands, isocyanides, and metal center. These results prompted us to perform a comparative study of bis(isothiocyanato)bis(trimethylphosphine) complexes of group 10 metals $M(NCS)_2(PMe_3)_2$, which have the same ligand set, toward the identical isocyanide CN–Ar (Ar = C_6H_3-2,6-*i*-Pr_2) (eqns (7)–(9)).

$Pd(NCS)_2(PMe_3)_2$ reacted with 2 equiv. of 2,6-diisopropyl phenyl isocyanide CN–Ar (Ar = C_6H_3-2,6-*i*-Pr_2) gave the bis(isocyanide) Pd(II) complex $[Pd(CN–Ar)_2(PMe_3)_2](SCN)_2$ (**16**), which was isolated as an orange solid and characterized by spectroscopy and elemental analysis (eqn (7)). However, repeated crystallizations of **16** from CH_2Cl_2/hexane caused the isocyanide dissociation and it went back to the starting material, suggesting that the steric congestion is due to the 2,6-diisopropyl groups in the CN–Ar ligand.

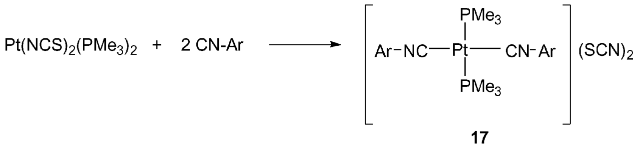


$$Pd(NCS)_2(PMe_3)_2 + 2\ CN\text{-}Ar \longrightarrow \left[Ar\text{-}NC\text{—}\overset{PMe_3}{\underset{PMe_3}{Pd}}\text{—}CN\text{-}Ar \right](SCN)_2 \xrightarrow[-\ 2\ CN\text{-}Ar]{} (Me_3P)_2Pd(N{=}C{=}S)_2$$

(Ar = C_6H_3-2,6-*i*-Pr_2)

16

(7)



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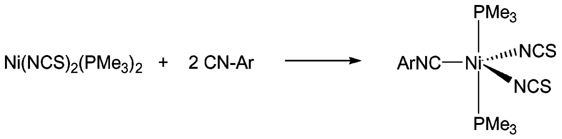
(8)



18

(9)

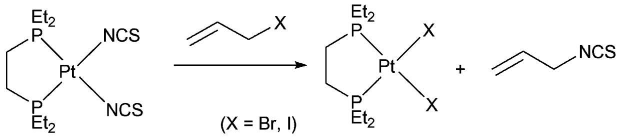
We also examined the corresponding reactions of the Pt and Ni analogues $M(NCS)_2(PMe_3)_2$ (M = Ni, Pt) with the isocyanide. Treating $Pt(NCS)_2(PMe_3)_2$ with 2 equiv. of 2,6-diisopropyl phenyl isocyanide produced the bis(isocyanide) Pt(II) complex $[Pt(CN–Ar)_2(PMe_3)_2](SCN)_2$ (**17**) as shown in eqn (8), in which the isocyanide dissociation did not occur. Isolated complexes **16** and **17** show two strong absorption bands at 2196 (C≡N) and 2055 (SCN) cm^{-1} (for **16**) and at 2195 (C≡N) and 2059 (SCN) cm^{-1} (for **17**), respectively. These IR data are well consistent with those for the bis(isocyanide) Pd(II) and Pt(II) complexes shown in eqns (4) and (5).

In contrast, the corresponding reaction of $Ni(NCS)_2(PMe_3)_2$ with 2 equiv. of 2,6-diisopropyl phenyl isocyanide resulted in the formation of the mono(isocyanide) 5-coordinate Ni(II) complex $[Ni(CN–Ar)(NCS)_2(PMe_3)_2]$ (**18**) (eqn (9)). Complex **18** was obtained as a brown solid in 91% yield. The IR spectrum of **18** also displays a stretching band at 2163 cm^{-1} due to C≡N and two strong bands at 2102 and 2047 cm^{-1} due to NCS of the complex and suggests a distorted TBP geometry. In addition, other spectral (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR) and analytical data strongly support the coordination of one isocyanide to the Ni metal. The present data indicate that the reactivity of group 10 metal bis(isothiocyanato) complexes $M(NCS)_2(PMe_3)_2$ toward $CN–C_6H_3$-2,6-*i*-Pr_2 depends primarily on the identity of the metal. However, we cannot underestimate the role of the steric bulk of the isocyanide due to the isopropyl groups on the phenyl ring.

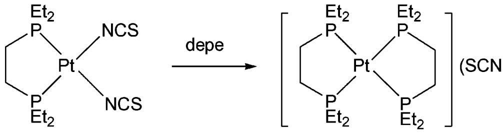
Properties of the group 10 bis(isothiocyanato) complexes with a chelating phosphine

We carried out reactions of the metal isothiocyanates with a chelating phosphine $M(NCS)_2L_2$ (M = Pd, Pt; L–L (depe) = $Et_2PCH_2CH_2PEt_2$) with CN–R, but the isocyanide coordination or any other adduct formation was not observed. Thus, we further examined the reactivity of these bis(isothiocyanato) complexes toward organic halides such as allyl halides (CH_2=CH–CH_2X; X = Br, I) and MeI.

Treatments of $Pd(NCS)_2(P(n\text{-}Pr)_3)_2$ and $Ni(NCS)_2(PMe_2Ph)_2$ with excess MeI and allyl iodide do not give any oxidative–addition products or metal-NCSR complexes as shown in Scheme 1. However, reactions of $Pt(NCS)_2$(depe) with excess allyl halides slowly proceeded to give the corresponding metal dihalo complexes as well as allyl isothiocyanate (CH_2=CH–CH_2–NCS), as shown in eqn (10), but other possible compounds such as oxidative–addition products were not observed. Interestingly, the GC–MS spectrum of the isolated allyl isothiocyanate revealed it to be a mixture of two linkage isomers, allyl isothiocyanate (CH_2=$CHCH_2$–NCS) and allyl thiocyanate (CH_2=$CHCH_2$–SCN). This linkage isomerism is believed to arise from the linkage isomerism in the starting materials. Integration ratios in $^{31}P\{^1H\}$ NMR spectra gave a strong clue to the presence of three linkage isomers, $Pt(NCS)_2L_2$, $Pt(SCN)_2L_2$, and $Pt(NCS)(SCN)L_2$, in the ratio of 1.00 : 0.77 : 0.84. Furthermore, the reaction of $Pt(NCS)_2$(depe) with depe in the mole ratio of 1 : 1 at room temperature slowly proceeded to give $[Pt(depe)_2](SCN)_2$ (**19**) in 91% yield as shown in eqn (11). Three absorption bands due to the terminal NCS or SCN groups appear at 2125, 2098, and 2056 cm^{-1} in the starting material $Pt(NCS)_2$(depe), whereas only a single band appears at 2052 cm^{-1} in the product (complex **19**). A single signal with satellites (J_{PtP} = 2124 Hz) in the $^{31}P\{^1H\}$ NMR of **19** strongly supports its high symmetry. The molecular structure of **19** (Fig. 8) clearly illustrates a symmetric square planar geometry, with the Pt atom on the crystallographic inversion center. The asymmetric unit of **19** consists of two halves of the formula unit with the other two halves generated by crystallographic inversion. The NCS^- ions are not coordinated to the Pt metal and act as counterions.



(10)



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(11)

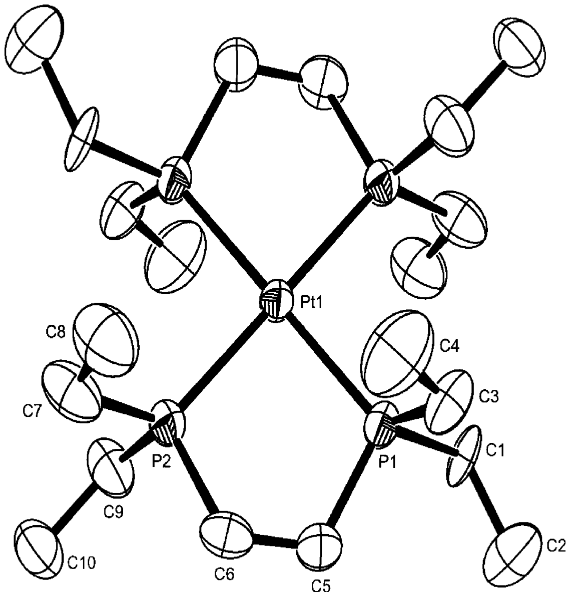

Fig. 8 ORTEP drawing[66] of **19**. Selected bond lengths (Å) and angles (°): Pt1–P2 2.3370(18), Pt1–P1 2.3446(17), Pt2–P3 2.3342(19), Pt2–P4 2.3475(18); P2#1–Pt1–P2 180.0, P2–Pt1–P1#1 84.41(6), P2–Pt1–P1 95.59(6), P1#1–Pt1–P1 180.0, P3–Pt2–P4 84.09(7). Symmetry transformations used to generate equivalent atoms: #1 = $-x$, $-y + 1$, $-z + 1$.

In summary, we have examined the reactivity bis(isothiocyanato)bis(phosphine) complexes of group 10 metals toward organic isocyanides. These complexes did not undergo cycloaddition with the isocyanides to give heterocyclic compounds. Instead, various unusual compounds were formed, depending on the isocyanide or supporting ligands. For Pd(II) and Pt(II) isothiocyanates, the mono(isocyanide) or bis(isocyanide) M(II) complexes, [M(CNR)(SCN)(NCS)L], $[M(CNR)(SCN)L_2](SCN)$, and $[M(CNR)_2L_2](SCN)_2$, were formed. Crystallographic data of several complexes clearly revealed the square planar geometry of the cationic parts of these complexes and the existence of SCN^- counterions. In particular, reactions of bis(isothiocyanato)Ni(II) complexes with organic isocyanides produced trigonal bipyramidal mono(isocyanide) Ni(II) complexes, which may be presumed to be a catalytic intermediate or precursor proposed in Ni-catalyzed isocyanide polymerization and olefin polymerization.

Experimental

All manipulations of air-sensitive compounds were performed under N_2 or Ar by Schlenk line techniques. Solvents were distilled from Na-benzophenone. The analytical laboratories at Basic Science Institute of Korea and Kangnung National University carried out elemental analyses. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectra were obtained on a JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si and to external 85% H_3PO_4. Conductivity data were obtained on a TPS 2100 conductivity bridge at 25 °C. Magnetic susceptibilities were measured with a Johnson Matthey MK–I magnetic balance, and magnetic moments were calculated from the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. $M(NCS)_2L_2$ (M = Ni, Pd, Pt; L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, $P(n\text{-}Pr)_3$, and depe = $Et_2PCH_2CH_2PEt_2$) were prepared by the literature method.[17] 2,6-Diisopropylphenyl isocyanide was prepared as described in the literature[64] and CN–C_6H_3-2,6-Me_2, CN-*t*-Bu and CN-*i*-Pr were purchased.

Reactions of $Ni(NCS)_2(PMe_2Ph)_2$ with isocyanides (CN–C_6H_3-2,6-Me_2 and CN-*t*-Bu)

To a Schlenk flask containing $Ni(NCS)_2(PMe_2Ph)_2$ (0.362 g, 0.80 mmol) were added sequentially CH_2Cl_2 (5 cm^3) and 2,6-dimethylphenyl isocyanide (0.210 g, 1.60 mmol). After stirring the reaction mixture at room temperature for 18 h, the solvent was removed completely, and the resulting residues were solidified with diethyl ether and CH_2Cl_2 (3 : 1) to give a crystalline brown solid. Recrystallization from CH_2Cl_2/ether gave dark red crystals of $Ni(NCS)_2(CN\text{–}C_6H_3\text{-}2,6\text{-}Me_2)(PMe_2Ph)_2$ (**1**, 0.422 g)

Complex **2** was prepared analogously.

Reaction of $Ni(NCS)_2(P(n\text{-}Pr)_3)_2$ with CN-*t*-Bu

To a Schlenk flask containing $Ni(NCS)_2(P(n\text{-}Pr)_3)_2$ (0.294 g, 0.59 mmol) were added CH_2Cl_2 (4 cm^3) and CN-*t*-Bu (0.134 cm^3, 1.18 mmol). After stirring the reaction mixture at room temperature for 18 h, the solvent was removed, and the resulting residues were solidified with diethyl ether to give a yellow solid, $[Ni(CN\text{-}t\text{-}Bu)_2(P(n\text{-}Pr)_3)_2](SCN)_2$(0.260 g). Repeated crystallization of $[Ni(CN\text{-}t\text{-}Bu)_2(P(n\text{-}Pr)_3)_2](SCN)_2$ from (diethyl ether)/CH_2Cl_2 gave a greenish yellow solid, $[Ni(P(n\text{-}Pr)_3)_2(CN\text{-}t\text{-}Bu)_3]^{2+}[Ni(1,3\text{-}\mu\text{-}NCS)(NCS)_3]_2^{2-}$ (0.181 g).

Reactions of $Pd(NCS)_2(P(n\text{-}Pr)_3)_2$ with CN-*t*-Bu and CN-*i*-Pr

To a Schlenk flask containing $Pd(NCS)_2(P(n\text{-}Pr)_3)_2$ (0.201 g, 0.37 mmol) were added CH_2Cl_2 (2 cm^3) and CN-*t*-Bu (0.088 cm^3, 0.78 mmol). The initial pale yellow solution slowly turned to a yellow solution. After stirring the reaction mixture for 18 h, the solvent was removed, and the resulting residues were solidified with diethyl ether. Recrystallization from diethyl ether gave yellow crystals of $Pd(NCS)(SCN)(CN\text{-}t\text{-}Bu)(P(n\text{-}Pr)_3)$ (**5**, 0.304 g).

Complex **6**, $\{Pd(CN\text{-}i\text{-}Pr)_2[P(n\text{-}Pr)_3]_2\}(SCN)_2$ was similarly prepared according to the procedure described above.

Reactions of $Pd(NCS)_2(PR_3)_2$ (PR_3 = PMe_3, PPh_2Me) with CN-*t*-Bu, CN-*i*-Pr and CN–C_6H_3-2,6-Me_2

To a CH_2Cl_2 (20 cm^3) suspension containing $Pd(NCS)_2(PMe_3)_2$ (0.284 g, 0.76 mmol) was added CN-*t*-Bu (0.180 cm^3, 1.59 mmol). The initial suspension instantly turned to a yellow solution, and then precipitation occurred. After stirring the reaction mixture for 18 h, the mixture was evaporated to give a crude solid, which was crystallized from CH_2Cl_2/hexane to give a yellow solid, $[Pd(CN\text{-}t\text{-}Bu)_2(PMe_3)_2](SCN)_2$ (**7**, 0.384 g).

Complexes **8–10** were prepared analogously.

Reactions of $Pt(NCS)_2(PR_3)_2$ (PR_3 = PMe_3, PEt_3, P(n-Pr)$_3$) with CN–C_6H_3-2,6-Me_2

To a CH_2Cl_2 (5 cm^3) suspension containing $Pt(NCS)_2(PMe_3)_2$ (0.199 g, 0.43 mmol) was added CN–C_6H_3-2,6-Me_2 (0.113 g, 0.86 mmol). The initial suspension instantly turned to a pale yellow solution. After stirring the reaction mixture for 18 h, the mixture was evaporated to give a crude solid. Recrystallization from CH_2Cl_2/diethyl ether gave yellow crystals of $[Pt(CN\text{–}C_6H_3\text{-}2,6\text{-}Me_2)_2(PMe_3)_2](SCN)_2$ (**11**, 0.212 g)

Complexes **12** and **13** were prepared analogously.

Reactions of $Pd(NCS)_2(PEt_3)_2$ with CN-*i*-Pr and CN–Ar (Ar = C_6H_3-2,6-Me_2)

To a CH_2Cl_2 (8 cm^3) solution containing $Pd(NCS)_2(PEt_3)_2$, (0.249 g, 0.54 mmol) was added CN-*i*-Pr (0.099 cm^3, 1.09 mmol) at room temperature. After stirring the reaction mixture for 18 h, the solvent was removed, and the resulting residues were solidified with diethyl ether to give a pale yellow solid, $[Pd(CN\text{–}R)(SCN)(PEt_3)_2](SCN)$ (R = *i*-Pr (**14**, 0.259 g).

Complex **15** was prepared analogously.

Reactions of $M(NCS)_2(PMe_3)_2$ (M = Pd, Pt, Ni) with CN–C_6H_3-2,6-*i*-Pr_2

To a CH_2Cl_2 (10 cm^3) suspension containing $Pd(NCS)_2(PMe_3)_2$ (0.241 g, 0.64 mmol) was added CN–C_6H_3-2,6-*i*-Pr_2 (0.268 cm^3, 1.41 mmol). The initial suspension instantly turned to an orange solution. After stirring the reaction mixture for 18 h, the mixture was evaporated to give a crude solid, which was washed with hexane. Recrystallization from CH_2Cl_2/hexane gave a yellow solid, $[Pd(CN\text{–}Ar)_2(PMe_3)_2](SCN)_2$ (**16**, 0.381 g). Several crystallizations from CH_2Cl_2/hexane caused the formation of $Pd(NCS)_2(PMe_3)_2$.

Complexes **17** and **18** were prepared analogously.

Reactions of $Pt(NCS)_2$(depe) with allyl bromide, allyl iodide, and depe

To a CH_2Cl_2 (3 cm^3) solution containing $Pt(NCS)_2$(depe) (0.347 g, 0.67 mmol) was added allyl bromide (0.811 g, 6.70 mmol). After stirring the reaction mixture for 18 h, the solvent was evaporated, and the resulting residues were solidified with diethyl ether to give a white solid, $PtBr_2$(depe). The solid was filtered, washed with diethyl ether and dried under vacuum (0.352 g, 94%). The collected filtrate was analyzed by GC and GC–MS. Reaction of $Pt(NCS)_2$(depe) with allyl iodide was analogously carried out.

To a CH_2Cl_2 (3 cm^3) suspension containing $Pt(NCS)_2$(depe) (0.169 g, 0.33 mmol) was added depe (0.074 g, 0.36 mmol). The initial suspension instantly turned to a colorless solution. After stirring the reaction mixture for 5 h, the mixture was evaporated to give a white solid, which was crystallized from CH_2Cl_2/hexane to give white crystals of $[Pt(depe)_2](SCN)_2$ (**19**, 0.170 g).

X-Ray structure determination

All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of SHELXTL programs.[65] All structures were solved by direct methods. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

For compound **12**, six carbon atoms (C25–C30) in one phosphine ligand showed extreme structural disorder and therefore were refined isotropically. For the same reason, the atoms (N2, C22, S2) in one of the NCS counterions for compound **19** were also refined isotropically. Details on crystal data, intensity collection, and refinement details are given in Table 2.

CCDC reference numbers 275741–275748.

See http://dx.doi.org/10.1039/b508134c for crystallographic data in CIF or other electronic format.

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References

1 G. Wilkinson, R. D. Gillard and J. A. McCleverty, *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1987, vol. 2, p 127.
2 J. L. Burmeister, *Coord. Chem. Rev.*, 1968, **3**, 225.
3 A. H. Norbury and A. J. P. Sinha, *Q. Rev. Chem. Soc.*, 1970, **24**, 69.
4 C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 1242.
5 J. J. MacDougall, A. W. Verstuyft, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1980, **19**, 1036; J. J. MacDougall, J. H. Nelson, M. W. Babich, C. C. Fuller and R. A. Jacobson, *Inorg. Chim. Acta*, 1978, **27**, 201.
6 G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.*, 1975, **97**, 1059; G. R. Clark, G. J. Palenik and D. W. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 1077; G. R. Clark and G. J. Palenik, *Inorg. Chem.*, 1970, **9**, 2754; G. Beran and G. J. Palenik, *Chem. Commun.*, 1970, 1355.
7 D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 5351.
8 A. J. Carty and A. Efraty, *Can. J. Chem.*, 1969, **47**, 2573.
9 I. Bertini and A. Sabatini, *Inorg. Chem.*, 1966, **5**, 1025.
10 J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587.
11 S. Hishi and M. Kato, *Inorg. Chem.*, 2003, **42**, 8728.
12 Y. S. Wong, S. Jacobson, P. C. Chieh and A. J. Carty, *Inorg. Chem.*, 1974, **13**, 284.
13 Yu. N. Kukushkin, L. V. Vrublevskaya, R. A. Vlasova, T. S. Isachukina, E. S. Postnikova and N. K. Sheleshkova, *Russ. J. Inorg. Chem.*, 1985, **30**, 224.
14 M. J. Coyer, M. Croft, J. Chen and R. H. Herber, *Inorg. Chem.*, 1992, **31**, 1752.
15 M. J. Coyer, R. H. Herber, J. Chen, M. Croft and S. P. Szu, *Inorg. Chem.*, 1994, **33**, 716.
16 S. A. Anderson, P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1976, 1959.
17 Y.-J. Kim, J.-T. Han, S. Kang, W. S. Han and S. W. Lee, *Dalton Trans.*, 2003, 3357.
18 H. Maciejewski, B. Marciniec, J. Gulinski, A. Karolak and N. K. Skvortsov, *Inorg. Chem. Commun.*, 2002, **5**, 464.
19 J. H. Lee, B.-S. Yoo and S. W. Lee, *Inorg. Chim. Acta*, 2001, **321**, 75.
20 H. Hou, P. K. Gantzel and C. P. Kubiak, *Organometallics*, 2003, **22**, 2817; G. M. Ferrence, E. Simón-Manso, B. K. Breedlove, L. Meeuwenberg and C. P. Kubiak, *Inorg. Chem.*, 2004, **43**, 1071; S. Hinze, J. K. Gong, P. E. Fanwick and C. P. Kubiak, *J. Organomet. Chem.*, 1993, **458**, C10; K. S. Ratliff, P. E. Fanwick and C. P. Kubiak, *Polyhedron*, 1990, **9**, 1487.
21 E. Boíllos and D. Miguel, *Organometallics*, 2004, **23**, 2568.
22 C. E. MacBeth, J. C. Thomas, T. A. Betley and J. C. Peters, , *Inorg. Chem.*, 2004, **43**, 4645.
23 A. F. G. Ribeiro, P. T. Gomes, A. R. Dias, J. L. Ferreira da Silva, M. T. Duarte, R. T. Henriques and C. Freire, *Polyhedron*, 2004, **23**, 2715.
24 M. Tanabiki, K. Tsuchiya, Y. Kumanomido, K. Matsubara, Y. Motoyama and H. Nagashima, *Organometallics*, 2004, **23**, 3976.
25 J.-S. Park, D.-H. Kim, S.-J. Kim, J. Ko, S. H. Kim, S. Cho, C.-H. Lee and S. O. Kang, *Organometallics*, 2001, **20**, 4483.
26 Y. Yamamoto, H. Takahata and F. Takei, *J. Organomet. Chem.*, 1997, **545**, 369; Y. Yamamoto, K. Ehara, K. Takahashi and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3376.
27 L. Ballester, S. Perez, A. Gutierrez, M. F. Perpiñan, E. Guitierrez-Puebla, A. Monge and C. Ruiz, *J. Organomet. Chem.*, 1991, **414**, 411.
28 E. Carmona, J. M. Marin, P. Palma and M. L. Poveda, *J. Organomet. Chem.*, 1989, **377**, 157.
29 D. Wilhekm, E. Wenschuh, U. Baumeister and H. Hartung, *Z. Anorg. Allg. Chem.*, 1994, **620**, 2114.
30 J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1090.
31 T. J. Deming and B. M. Novak, *J. Am. Chem. Soc.*, 1993, **115**, 9101.
32 M. Monfort, C. Bastos, C. Diaz, J. Ribas and X. Solans, *Inorg. Chim. Acta*, 1994, **218**, 185; M. Monfort, J. Ribas and X. Solans, *Inorg. Chem.*, 1994, **33**, 4271.
33 A. Escuer, S. B. Kumar, F. Mautner and R. Vicente, *Inorg. Chim. Acta*, 1998, **269**, 313; R. Vicente, A. Escuer, J. Rivas and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1994, 259.
34 T. Rojo, R. Cortes, L. Lezama, M. I. Arriortua, K. Urtiaga and G. Vilenueve, *J. Chem. Soc., Dalton. Trans.*, 1991, 1779.
35 M. D. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2929.
36 A. E. Shvelashvili, M. A. Porai-Koshity and A. S. Antsyshkins, *J. Struct. Chem.*, 1969, **10**, 552.
37 B. Żurowska, J. Mroziński, M. Julve, F. Lloret, A. Maslejova and W. Sawka-Dobrowolska, *Inorg. Chem.*, 2002, **41**, 1771.
38 T. K. Maji, I. R. Laskar, G. Mostafa, A. J. Welch, P. S. Mukherjee and N. R. Chaudhuri, *Polyhedron*, 2001, **20**, 651.
39 S. Trofimenko, J. C. Calabrese, J. K. Kochi, S. Wolowice, F. B. Hulsbergen and J. Reedijk, *Inorg. Chem.*, 1992, **31**, 3943.
40 A. P. Ginsberg, R. C. Sherwood, R. W. Brookes and R. L. Martin, *J. Am. Chem. Soc.*, 1971, **93**, 5927.
41 M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3277.
42 J. M. Shi, C. Y. Shu, W. T. Yu, K. J. Sun, C. J. Wu and J. J. Lu, *Pol. J. Chem.*, 2001, **75**, 1067.
43 R. Cortés, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Uritaga and M. I. Arriortua, *J. Chem. Soc., Dalton. Trans.*, 1992, 2723.
44 J.-C. Liu, Y. Song, J.-Z. Zhuang, X.-Z. You, X.-Y. Huang and Z.-X. Huang, *Jiegou Huaxue*, 2000, **19**, 81.
45 J. Cano, G. De Munno, F. Lloret and M. Julve, *Inorg. Chem.*, 2000, **39**, 1611.
46 J. L. Burmeister, T. P. O'sullivan and K. A. Johnson, *Inorg. Chem.*, 1971, **10**, 1803.
47 M. Nonoyama, *Inorg. Chim. Acta*, 1976, **20**, 53.
48 U. A. Gregory, J. A. Jarvis, B. T. Kilbourn and P. G. Owston, *J. Chem. Soc. A*, 1970, 2770.
49 B. Crociani, T. Boschi and U. Belluco, *Inorg. Chem.*, 1970, **9**, 2021; T. Boschi, B. Crociani and U. Belluco, *Inorg. Chim. Acta*, 1975, **12**, 39.
50 W. J. Cherwinski, H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 1511.
51 J. S. Miller and A. L. Balch, *Inorg. Chem.*, 1972, **11**, 2069; J. R. Boehm and A. L. Balch, *J. Organomet. Chem.*, 1976, **112**, C20; A. L. Balch, J. R. Boehm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431; J. R. Boehm, D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 4845; M. M. Olmstead, H. Hope, L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, 1977, **99**, 3502.
52 D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg and J. S. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 1961; S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, 1976, **15**, 535.
53 M. F. Rettig, E. A. Kirk and P. M. Maitlis, *J. Organomet. Chem.*, 1976, **111**, 113.
54 K. R. Nagasundara, N. M. Nanje Gowda and G. K. N. Reddy, *J. Organomet. Chem.*, 1977, **129**, 121.
55 H. Ogawa, T. Joh and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1988, 561; K. Onitsuka, K. Yanai, F. Takei, T. Joh and S. Takahashi, *Organometallics*, 1994, **13**, 3862; K. Onitsuka, T. Joh and S. Takahashi, *J. Organomet. Chem.*, 1994, **464**, 247.
56 Y. Yamamoto, *Yuki Gosei Kagaku Kyokaishi*, 1993, **51**, 804; Y. Yamamoto and H. Yamazaki, *Organometallics*, 1993, **12**, 933.
57 P. Espinet, J. Fornies, C. Fortuño, G. Hidalgo, F. Martinez, M. Tomas and A. J. Welch, *J. Organomet. Chem.*, 1986, **317**, 105.
58 R. Usón, J. Fornies, P. Espinet, F. Martinez, C. Fortuño and B. Menjon, *J. Organomet. Chem.*, 1983, **256**, 365.
59 J. G. P. Delis, P. G. Aubel, K. Vrieze, P. W. N. M. Van Leeuwen, N. Veldman, A. L. and F. J. R. van Neer, *Organometallics*, 1997, **16**, 2948.
60 J. Vicente, J. A. Abad, W. Förtsch, P. G. Jones and A. K. Fischer, *Organometallics*, 2001, **20**, 2704; J. Vicente, J. A. Abad, A. D. Frankland, J. Lopez-Serrano, M. C. Ramirezde Arellano and P. G. Jones, *Organometallics*, 2002, **21**, 272; J. Vicente, I. Saura-Llamas, C. Grünwald, C. Alcaraz, P. G. Jones and D. Bautista, *Organometallics*, 2002, **21**, 3587; J. Vicente, J. A. Abad, E. Martinez-Viviente and P. G. Jones, *Organometallics*, 2002, **21**, 4454; J. Vicente, J. A. Abad, E. Martinez-Viviente and P. G. Jones, *Organometallics*, 2003, **22**, 1967; J. Vicente, J. A. Abad, R. Clemente, J. Lopez-Serrano, M. C. Ramirez de Arellano, P. G. Jones and D. Bautista, *Organometallics*, 2003, **22**, 4248; J. Vicente, J. A. Abad, F. S. Hernandez-Mata, B. Rink, P. G. Jones and M. C. Ramirez de Arellano, *Organometallics*, 2004, **23**, 1292; J. Vicente, J. A. Abad, M. J. Lopez-Saez, W. Förtsch and P. G.

Jones, *Organometallics*, 2004, **23**, 4414; J. Vicente, J. A. Abad, J. Lopez-Serrano and P. G. Jones, *Organometallics*, 2004, **23**, 4711; J. Vicente, A. Arcas, J. M. Fernandez-Hernandez, D. Bautista and P. G. Jones, *Organometallics*, 2005, **24**, 2516.
61 H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 503.
62 P. M. Treichel, W. J. Knebel and R. W. Hess, *J. Am. Chem. Soc.*, 1971, **93**, 5424.
63 H. Crociani, M. Nicolini and R. L. Richards, *Inorg. Chim. Acta*, 1975, **12**, 53.
64 W. P. Weber and G. W. Gokel, *Tetrahedron Lett.*, 1972, 1637.
65 G. M. Sheldrick, *SHELX-97*, University of Gttingen, Germany, 1997.
66 L. J. Farrugia, *ORTEP-3 for Windows*, University of Glasgow, 1997.