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Alkylidenes by α-H Abstraction from Metallacycles. Synthesis and Characterization of Alkylidene-Bridged Complexes of Nickel

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The 16e$^-$ pseudoallylic complex $\mathrm{Ni(\eta^3\text{-}CH_2C_6H_4}\text{-}o\text{-}\mathrm{Me)Cl(PMe_3)}$ effects α-C–H abstraction from the benzoannelated nickelacycle $\overline{\mathrm{Ni(CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)(PMe_3)_2}$ **(1)** under very mild conditions, with formation of the tetrametallic species $[\overline{\mathrm{Ni_2(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)(PMe_3)_2]_2(\mu\text{-}Cl)_2}$ **(2)**, in which two identical metal–metal-bonded bimetallic subunits are held together by chloride bridges. Each of these moieties incorporates a bifunctional organic fragment that possesses alkylidene and aryl termini that bridge the two metal atoms. Rupture of the $\mathrm{(Ni_2)_2}$-$(\mu\text{-}\mathrm{Cl})_2$ bridges by PMe$_3$ produces a binuclear nonsymmetric alkylidene, $\overline{\mathrm{Ni_2(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)Cl(PMe_3)_3}$ **(3)**, also exhibiting alkylidene and aryl bridges. A similar reaction of **2** with $\mathrm{Me_2PCH_2CH_2PMe_2}$ (dmpe) furnishes the related, albeit cationic, alkylidene species $[\overline{\mathrm{Ni_2(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)(dmpe)_2]Cl}$ **(4)**. Interaction of the tetranuclear alkylidene **2** with NaCp produces the bimetallic product $\mathrm{Cp}\overline{\mathrm{Ni(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)Ni(PMe_3)_2}$ **(5)**. This complex can also be obtained by α-H abstraction from the methylene group of the metallacycle **1** by the 18-electron allyl derivative $\mathrm{CpNi(\eta^3\text{-}C_3H_5)}$. The former reaction route also allows the synthesis of the analogous derivatives $\mathrm{(C_5H_4R)}\overline{\mathrm{Ni(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)Ni(PMe_3)_2}$ (R = Me **(6)**, *i*-Pr **(7)**). Different kinds of μ-alkylidene compounds are furnished by the reaction of **2** and the poly(pyrazolyl)borate salts $\mathrm{K[HB(pz)_3]}$ (pz = pyrazolyl) and $\mathrm{Tl[H_2B(3\text{-}}t\mathrm{\text{-}Bu\text{-}pz)_2]}$. These new complexes have η^2-bonded poly(pyrazolyl)borate ligands that bridge the two Ni atoms, i.e. $\overline{\mathrm{Ni_2(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)[\mu_2\text{-}\eta^1{:}\eta^1\text{-}HB(pz)_3](PMe_3)_2}$ **(8)** and $\overline{\mathrm{Ni_2(\mu_2\text{-}CHCMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)[\mu_2\text{-}\eta^1{:}\eta^1\text{-}H_2B(3\text{-}}t\mathrm{\text{-}Bu\text{-}pz)_2](PMe_3)_2}$ **(9)**, respectively. Complexes **2** and **3** have been characterized by X-ray crystallography. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with a = 9.815(4) Å, b = 10.550(4) Å, c = 19.669(7) Å, β = 104.39(3)°, and Z = 4. Crystals of **3** are orthorhombic, *Pbca*, with a = 17.152(4) Å, b = 18.431(3) Å, c = 32.577(5) Å, and Z = 16. Both display short metal–metal contacts (2.384(3) and 2.393(3) Å, respectively) suggestive of strong Ni–Ni bonding interactions. The alkylidene fragment symmetrically bridges the two Ni atoms in **2** and **3**, but while in **2** the aryl bridges are also symmetric, in **3** one of the Ni–C$_{\mathrm{aryl}}$ distances at 2.17(1) Å is perceivably longer than the other (1.99(2) Å). Compound **5** has also been characterized by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/n$, with unit cell constants a = 9.013(2) Å, b = 16.675(2) Å, c = 15.291(7) Å, β = 91.04(3)°, and Z = 4.

Alkylidene complexes of the transition metals are a prominent class of organometallic compounds, and their participation in a number of important stoichiometric and catalytic reactions is now well documented.[2] Mononuclear alkylidenes have been known for many years, having been discovered by Fischer and Maasböl in 1964.[3] In contrast, μ-alkylidenes in which the carbene ligand bridges two metal centers have only been prepared and investigated in more recent times,[2,4] interest in these compounds arising because of their proposed involvement in Fischer–Tropsch synthesis, olefin metathesis reactions, and Ziegler–Natta catalysis.[2]

Alkylidene compounds can be made, among other methods,[2] by α-H abstraction from transition-metal alkyls,[5] a process that has attracted considerable attention in current years. Both intramolecular and intermolecular

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(1) (a) Universidad de Sevilla-CSIC. (b) CSIC and Universidad Complutense.

(2) (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982,** *20,* 159. (b) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986,** *25,* 121. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984,** *31,* 205. (d) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 587. (e) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987,** *87,* 411. (f) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Chapter 3, pp 221–284. Dötz, K. H. *Ibid.*, Chapter 4, pp 285–370. (g) Dötz, K. H. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

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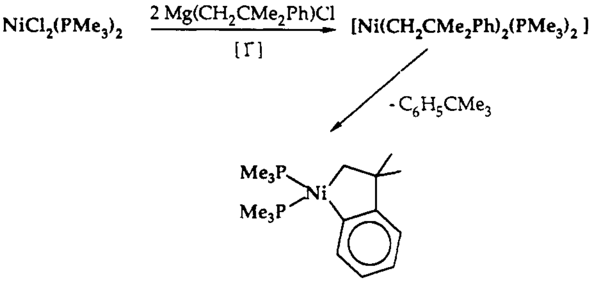
pathways have been positively identified, and the fate of the abstracted hydrogen atom has been frequently used as an important mechanistic probe. This reaction is well substantiated for compounds of the early transition metals,[5] and recent studies suggest that complexes of the late transition metals are also susceptible to this transformation.[6] The presence of at least one metal–alkyl functionality in the majority of the simple metallacycles offers the possibility of using these species as attractive starting materials for the synthesis of transition-metal alkylidenes. Nevertheless, and although β-H elimination from metallacycles has traditionally been assumed to be the initial step in their thermolysis reactions,[7] analogous α-H abstractions are rare[8] and to our knowledge stable alkylidene complexes have not been obtained from metallacycles as a result of such a H-elimination reaction. In this contribution we wish to report that in the presence of suitable reagents, the benzoannelated nickelacycle[9] $Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$ (1) undergoes a clean α-H abstraction to afford a tetrametallic species of composition $[Ni_2(CHCMe_2\text{-}o\text{-}C_6H_4)Cl(PMe_3)_2]_2$ (2). This contains two pairs of metal–metal-bonded Ni_2 units in which the two Ni centers are bridged by an alkylidene and an aryl ligand. The syntheses of other related binuclear Ni_2 alkylidenes and some characteristic reactivities are also reported. Part of this work has been briefly communicated.[10]

Results

Synthesis and Structural Characterization of the Tetrametallic, Alkylidene-Bridged Complex $[Ni_2(\mu_2\text{-}CHCMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2]_2(\mu\text{-}Cl)_2$ (2).

We have recently shown that the I⁻-catalyzed alkylation of $NiCl_2(PMe_3)_2$, using $Mg(CH_2CMe_2Ph)Cl$ as the alkylating reagent, yields the benzonickelacyclopentene complex[9] $Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$ (1). This reaction has been found to occur with δ-H abstraction from an unstable dialkyl, as illustrated in Scheme I. We have subsequently developed a large body of insertion chemistry[11] based on 1, and this has required the synthesis of multigram quantities of this complex. During these large-scale preparations, the formation of small amounts (~1%) of a dark red, sparingly soluble microcrystalline solid (2) has been noticed in some instances. This byproduct appears usually at the late stages of the workup procedure, and this fact, coupled with the analytical figures obtained for 2, which indicate a lower phosphorus content than in 1, suggests that 2 may be derived from 1 by a more or less complex phosphine abstraction reaction. This assumption was also in agreement with the known substitution chemistry of the nickelacycle, since this compound has one very labile PMe_3 ligand that can be readily substituted by other donor molecules.[9,12]

Scheme I



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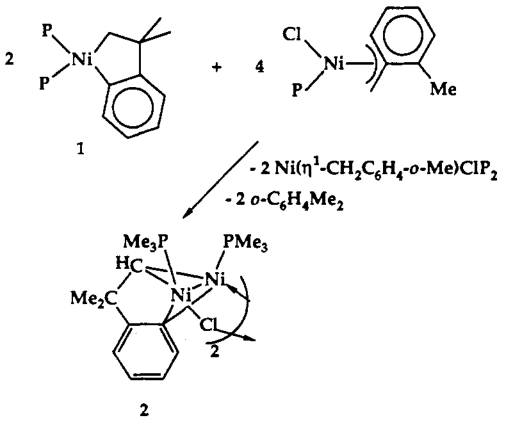
To test this hypothesis, we have carried out the reaction of 1 with the η^3-benzyl derivative $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}CH_3)Cl(PMe_3)$, which by virtue of the relatively weak Ni–pseudoallyl interaction cleanly and fastly captures PMe_3[13] (to yield the corresponding η^1-benzyl $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}CH_3)Cl(PMe_3)_2$) and therefore acts as a very effective "PMe_3 sponge". This experiment proved successful, and in accord with our expectations the formation of crystalline 2 followed upon mixing toluene solutions of 1 and of the η^3-*o*-xylyl complex. In addition, $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}CH_3)Cl(PMe_3)_2$ was also formed but approximately half the starting metallacycle remained unreacted, thus indicating the correct stoichiometry to be 1:2, as shown in eq 1. A closer inspection of the reaction mixture reveals the additional formation of $o\text{-}C_6H_4Me_2$ (GC–MS). Hence, in addition to capturing the leaving PMe_3 group, the



(1)

---

(3) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(4) For some examples see: (a) Bullock, R. M.; Hembre, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7868. (b) Denise, B.; Navarre, D.; Rudler, H. *J. Organomet. Chem.* **1989**, *375*, 273. (c) Minghetti, G.; Albinati, A.; Bandini, A. L.; Banditelli, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 120. (d) Noh, S. K.; Heintz, R. A.; Janiak, C.; Sendlinger, S. C.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 775. (e) Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2469. (f) Bandy, J. A.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2477.

(5) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (c) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (d) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (e) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

(6) See for example: (a) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620. (b) Fryzuk, M. D.; Joshi, K. *J. Am. Chem. Soc.* **1989**, *111*, 4498.

(7) (a) Grubbs, R. H.; Miyashita, A.; Liu, M.-I.M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (b) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418. (c) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. (d) Fischer, W.; Hembre, R. T.; Sidler, D. R.; Norton, J. R. *Inorg. Chim. Acta* **1992**, *198–200*, 57.

(8) (a) Puddephatt, R. J. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 353. (b) Burton, J. T.; Puddephatt, J. R. *Organometallics* **1986**, *5*, 1312. (c) Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 3973.

(9) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruíz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883.

(10) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1991**, 148.

(11) (a) Cámpora, J.; Carmona, E.; Palma, P.; Poveda, M. L. *J. Chem. Soc., Perkin Trans.* **1990**, 180. (b) Cámpora, J.; Llebaría, A.; Moretó, J. M.; Poveda, M. L.; Carmona, E. *Organometallics*, in press. (c) Cámpora, J.; Poveda, M. L.; Carmona, E., to be submitted for publication.

(12) Carmona, E.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *Polyhedron* **1989**, *8*, 1069.

(13) Carmona, E.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.

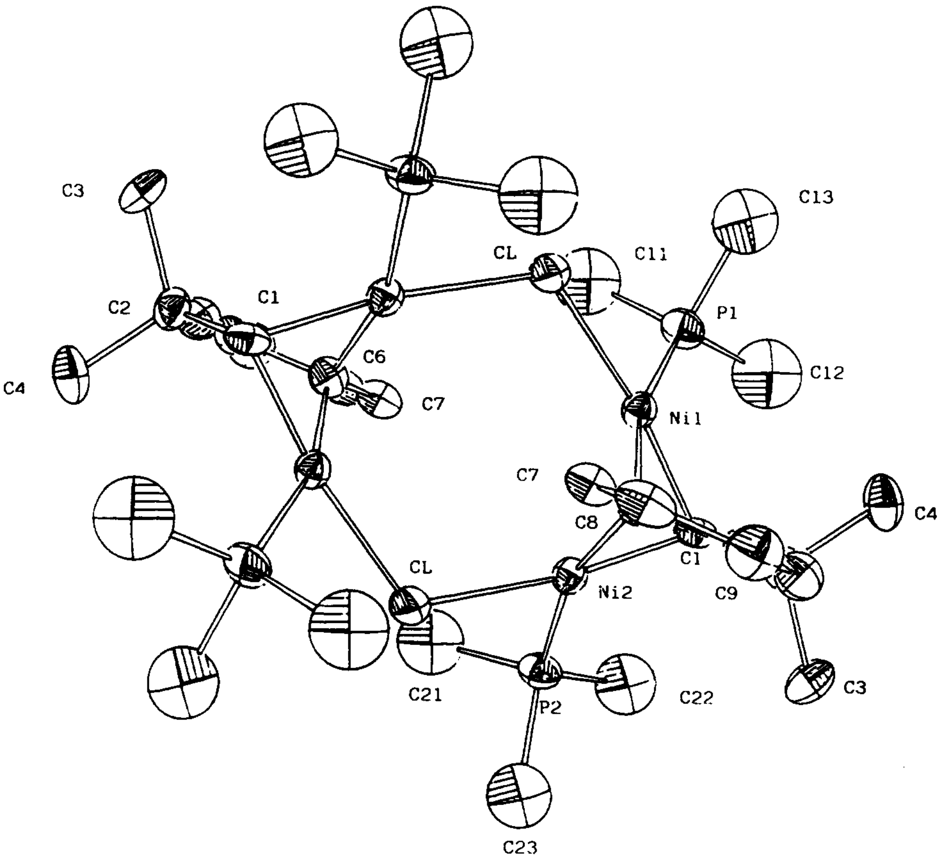


Figure 1. Molecular structure of the bridging alkylidene derivative 2 with the thermal ellipsoids shown at 50% probability. The Ni–Ni bonds have been omitted for clarity.

pseudoallyl complex abstracts one of the methylenic hydrogen atoms of the already metalated organic fragment to afford an alkylidene functionality.

Complex 2 is a dark red, almost black, crystalline species. As a highly crystalline material it can be handled in air for short periods of time, but it decomposes quickly when in the form of a finely divided solid. In solution it is very unstable toward oxygen and moisture and undergoes fast decomposition in contact with the atmosphere. It shows poor solubility in most common organic solvents, but it is sufficiently soluble in CD_3CN to allow investigation of its NMR properties. Although some information about its structure can be obtained from spectroscopic studies, its molecular complexity was determined by a single-crystal X-ray analysis.

Figure 1 shows an ORTEP perspective view of the molecule of 2, while Figure 2 gives a clear picture of one of the symmetry-related Ni_2 subunits. Table I collects important bond distances and angles. As can be seen, the solid-state structure of 2 possesses a center of symmetry that relates the two binuclear units of the planar, six-membered Ni_4Cl_2 ring. Similar planar M_4Cl_2 rings have been found in somewhat related structures, e.g. $[Ni_2(\mu_2\text{-}C_3Cl_3)(CO)_2(\mu\text{-}Cl)]_2$[14] and $[Pd_2(CHC_6H_4NMe_2\text{-}2)(SEt_2)\text{-}(\mu\text{-}Cl)(\mu'\text{-}Cl)]_2$, the latter containing also a bridging alkylidene ligand.[15] The two Ni–Cl distances in 2 are identical within experimental error (2.301(6) and 2.306(6) Å) and have values similar to those found in the already mentioned $[Ni_2(\mu_2\text{-}C_3Cl_3)(CO)_2(\mu\text{-}Cl)]_2$ complex (2.237(1) Å, average). The most relevant feature in the structure of 2 is doubtless the existence of metal–metal-bonded Ni_2 subunits, which are bridged by an alkylidene and an aryl group, both belonging to the same organic fragment, namely one derived from the original neophyl ligand by successive loss of two H atoms. Bridging alkylidene structures are relatively few, as compared to the large number of terminal alkylidenes that are presently known.[2c] For the homobimetallic alkylidene functionality existing in 2, the coordination is symmetrical (Ni(1)–C(1) and Ni-

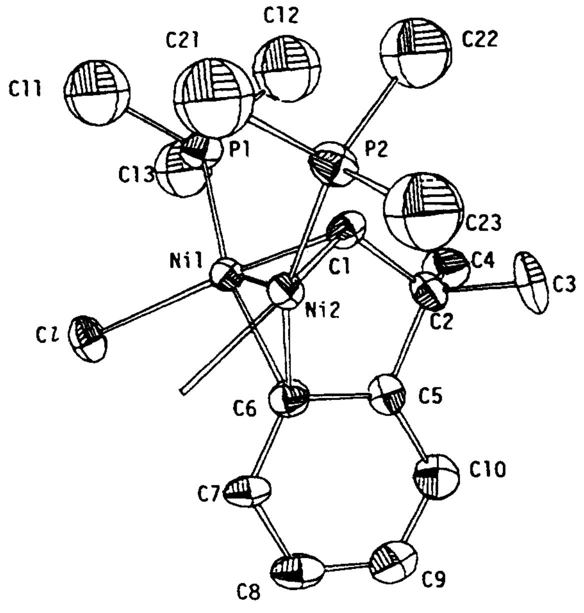


Figure 2. ORTEP diagram for 2 showing the thermal ellipsoids at 50% probability and giving the atom-labeling scheme. Only half of the molecule has been represented, and all H atoms have been omitted.

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[14] Frisch, P. D.; Posey, R. G.; Khare, G. P. *Inorg. Chem.* **1978**, *17*, 402.

[15] Maassarani, F.; Pfeffer, M.; Spek, A. L.; Schreurs, A. M. M.; van Koten, G. *J. Am. Chem. Soc.* **1986**, *108*, 4222.

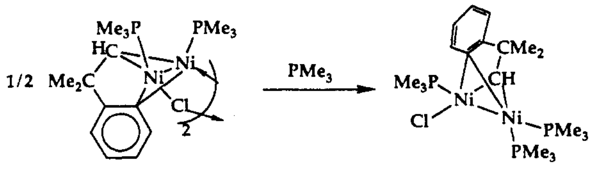
Table I. Selected Bond Distances (Å) and Angles (deg) for 2

Ni1–Ni2	2.384(3)	P2–C22	1.81(4)
Ni1–Cl	2.306(6)	P2–C23	1.78(3)
Ni1–P1	2.180(6)	C1–C2	1.49(3)
Ni1–Cl	1.91(2)	C2–C3	1.55(3)
Ni1–C6	2.04(2)	C2–C4	1.58(2)
Ni2–P2	1.175(6)	C2–C5	1.55(3)
Ni2–Cl	2.301(6)		
Ni2–Cl	1.90(2)	C5–C6	1.42(3)
Ni2–C6	2.90(2)	C5–C10	1.39(3)
P1–C11	1.74(4)	C6–C7	1.39(3)
P1–C12	1.79(5)	C7–C8	1.37(3)
P1–C13	1.71(3)	C8–C9	1.39(4)
P2–C21	1.78(4)	C9–C10	1.35(4)
C1–Ni1–C6	75.8(8)	C1–C2–C5	102.1(16)
P1–Ni–C6	164.4(6)	C1–C2–C4	112.1(17)
P1–Ni–C1	94.7(6)	C1–C2–C3	112.8(18)
Cl–Ni1–C6	97.5(6)	C4–C2–C5	110.0(16)
Cl–Ni1–C1	170.9(6)	C3–C2–C5	110.9(18)
Cl–Ni1–P1	93.2(2)	C3–C2–C4	108.9(18)
Ni2–Ni1–C6	54.6(6)	C2–C5–C10	125.3(18)
Ni2–Ni1–C1	51.0(6)	C2–C5–C6	113.3(17)
Ni2–Ni1–P1	128.1(2)	C6–C5–C10	121.4(18)
Ni2–Ni1–Cl	120.1(2)	Ni2–C6–C5	103.4(14)
Ni1–Ni2–C6	54.2(6)	Ni1–C6–C5	104.1(14)
Ni1–Ni2–C1	51.4(6)	Ni1–C6–Ni2	71.2(7)
Ni1–Ni2–P2	130.6(2)	C5–C6–C7	115.5(17)
C1–Ni2–C6	75.9(8)	Ni2–C6–C7	126.5(14)
P2–Ni2–C6	163.6(1)	Ni1–C6–C7	127.2(15)
P2–Ni2–C1	95.8(6)	C6–C7–C8	122.6(20)
Ni1–C1–Ni2	77.6(7)	C7–C8–C9	120.0(20)
Ni2–C1–C2	110.7(14)	C8–C9–C10	119.7(22)
Ni1–C1–C2	110.2(14)	C5–C10–C9	120.7(22)

(2)–C(2) bond lengths of 1.91(2) and 1.90(2) Å, respectively). An interesting aspect of bridging alkylidene structures is that the M–C–M internal angle is essentially constant (in the range 75–82°) regardless of the specific peculiarities of the complexes considered,[2c] and this has been associated with alkylidene enhancement of the M–M bonding by removal of antibonding electrons.[2c] This is particularly significant for elements, such as Ni, with high electron counts. In 2 this angle is 77.6(7)°, well within the expected range. The Ni(1)–Ni(2) bond length of 2.384(3) Å is denotative of a strong interaction between the two metal centers. In the absence of steric constraints, the length of a Ni–Ni single bond has been estimated[16] to be in the range 2.32–2.36 Å,[17] although due to a variety of factors longer Ni–Ni bonds are not unusual.[14,18] In fact, Jones and co-workers have shown that Ni–Ni distances may be rationalized in terms of variations in the electron counts of the metals, the type of bridging atoms, and the nature of the coligands.[18a] The Ni–Ni bond in 2 is bridged by an essentially planar $CHC(Me)_2C_6H_4$ chain, which adopts an almost perpendicular orientation with respect to the Ni–Ni vector and which acts as a bidentate ligand through the alkylidene and the ortho aryl carbons. The coordination of the aryl is symmetrical, the Ni(1)–C(6) and Ni(2)–C(6) bond distances being equal within experimental error (2.04(2) and 2.05(2) Å, respectively). These distances compare favorably with those found in other Ni compounds containing bridging aryl ligands.[19] As in the majority of complexes that have this type of functionality,[20] the aryl ring is roughly perpendicular to the axis joining the two bridged metals.[21] The coordination sphere around each nickel center is completed by a PMe_3 group, approximately trans with respect to the bridging aryl carbon (C(6)–Ni(1)–P(1) = 164.4(6)°; C(6)–Ni(2)–P(2) = 163.6(1)°). By and large, and as is depicted in Figure 2, the geometry of the binuclear subunits present in 2 closely resembles the well-known A-frame type structures.[22]

As mentioned above, compound 2 is sufficiently soluble in CH_3CN (from which solutions it can be recovered as an oily material by evaporation under vacuum) to allow its characterization by NMR methods. Whether the Ni_4Cl_2 structure is maintained in solution cannot be fully ascertained, since splitting of the chloride bridges by CD_3CN is not to be excluded in view of the facility with which 2 reacts with donor ligands (vide infra). Irrespective of this, the NMR data obtained for 2 are clearly in accord with the structural features intrinsic to the binuclear moieties. As an example, the μ_2-CHR proton appears as a triplet ($^3J_{HP}$ = 14.3 Hz), due to the coupling with two equivalent ^{31}P nuclei at the fairly high-field value of 3.45 ppm, and the Ni-bonded alkylidene carbon resonates at 120.2 ppm. The latter resonance is in the range expected for the deshielded alkylidene carbon[2a,c,23] in M–M-bonded bridging alkylidenes (ca. 200–90 ppm).

Reaction of 2 with Phosphines and Anionic Nucleophiles: Formation of New Alkylidene Complexes. Disruption of the chloride bridges in 2 may be effected by addition of P-donor ligands. Thus, treatment of 2 with 2 mol equiv of PMe_3 affords the dark red binuclear alkylidene 3 (eq 2) in relatively low yields. Compound 3



2 3 (2)

is a rather unstable species that disproportionates slowly in solution to a mixture of 2 and an ylide complex of composition $\overline{Ni[C(H)(PMe_3)CMe_2C}_6H_4]Cl(PMe_3)$.[24] This, coupled with its propensity to react with additional amounts of PMe_3 to afford the already mentioned ylidic species, explains the low, isolated, yields of this product. Despite its instability, 3 has been fully characterized by elemental analysis, spectroscopy, and X-ray studies.

Figure 3 shows an ORTEP perspective view of one of the two independent molecules of 3 that exist in the unit cell, along with the atom-numbering scheme. Table II contains important bond distances and angles. From a structural viewpoint, compound 3 is a rather unusual member of this class of bridging alkylidenes since, despite being homometallic, it contains two different fragments. With few exceptions, all known homobimetallic μ-alkylidene compounds are symmetric.[2c] Not surprisingly, the

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[16] Adams, R. D.; Cotton, F. A.; Rusholme, R. A. *J. Coord. Chem.* **1971**, *1*, 275.

[17] Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 712.

[18] (a) Jones, R. A.; Whittlesey, B. R. *Inorg. Chem.* **1986**, *25*, 852 and references therein. (b) Manojlovic-Muir, L.; Muir, K. W.; Davis, W. M.; Mirza, H. A.; Puddephatt, R. J. *Inorg. Chem.* **1992**, *31*, 904.

[19] Bennett, M. A.; Griffiths, K. D.; Okano, T.; Parthasarathi, V.; Robertson, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 7047.

[20] (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (b) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1991**, *10*, 171.

[21] For structures with different geometries see: (a) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397. (b) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.

[22] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 19.

[23] (a) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319. (b) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345. (c) Baxter, S. M.; Wolczanski, P. T. *Organometallics* **1990**, *9*, 2498.

[24] Belderraín, T. R.; Monge, A.; Nicasio, M. C.; Paneque, M.; Poveda, M. L.; Ruiz, C.; Carmona, E., to be submitted for publication.

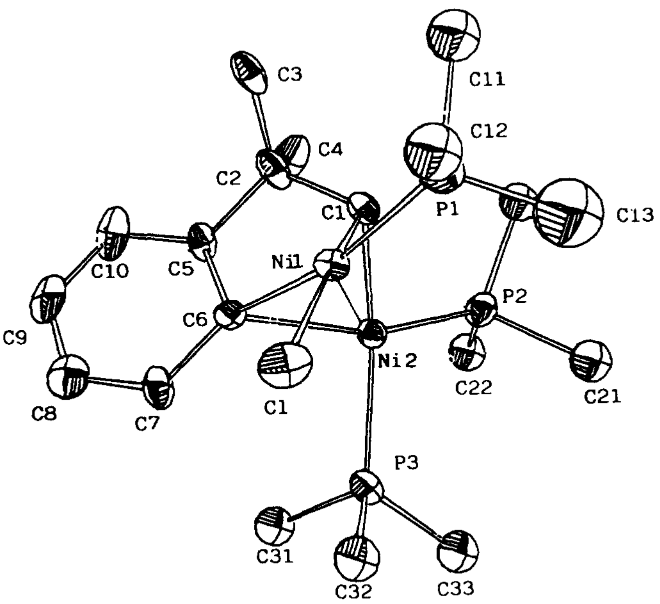


Figure 3. ORTEP representation for 3 showing the thermal ellipsoids at 50% probability and giving the atom-labeling scheme.

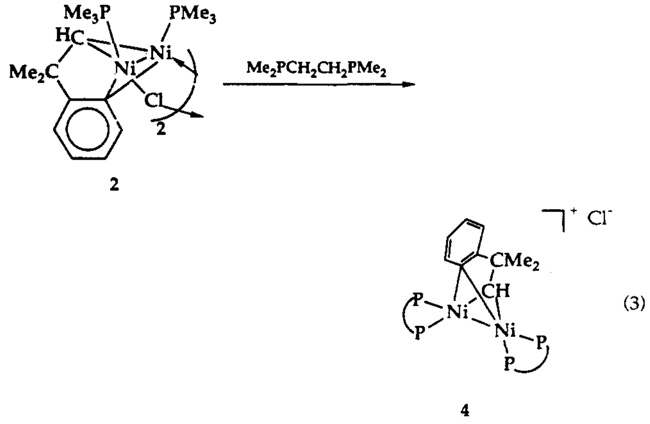
Table II. Selected Bond Distances (Å) and Angles (deg) for 3

	molecule A	molecule B		molecule A	molecule B
Ni1–Ni2	2.384(3)	2.403(3)	C2–C3	1.56(2)	1.51(3)
Ni1–P1	2.182(5)	2.157(6)	C2–C4	1.56(2)	1.53(3)
Ni1–Cl1	2.262(6)	2.256(6)	C2–C5	1.52(2)	1.51(3)
Ni1–C1	1.95(1)	1.92(2)	C5–C6	1.41(2)	1.37(2)
Ni1–C6	1.99(2)	2.00(2)	C5–C10	1.36(2)	1.40(3)
Ni2–P2	2.136(5)	2.160(6)	C6–C7	1.43(2)	1.43(3)
Ni2–P3	2.244(5)	2.231(6)	C7–C8	1.37(3)	1.38(3)
Ni2–C1	1.92(1)	1.87(2)	C8–C9	1.35(3)	1.36(4)
Ni2–C6	2.17(1)	2.19(2)	C9–C10	1.38(3)	1.35(4)
C1–C2	1.54(2)	1.52(3)			
C1–Ni1–C6	77.9(6)	77.0(7)	P2–Ni2–P3	100.0(2)	99.2(2)
Cl1–Ni1–C6	97.9(5)	97.1(5)	Ni2–C1–C2	108(1)	110(1)
Cl1–Ni1–C1	174.4(5)	171.8(5)	Ni1–C1–C2	107(1)	108(1)
P1–Ni1–C6	169.6(5)	166.2(5)	C1–C2–C5	106(1)	104(2)
P1–Ni1–C1	93.6(5)	93.3(5)	C1–C2–C4	110(1)	109(2)
P1–Ni1–Cl1	91.0(2)	93.5(2)	C1–C2–C3	111(1)	111(2)
Ni2–Ni1–C6	58.8(5)	58.7(5)	C4–C2–C5	112(1)	111(2)
Ni2–Ni1–C1	51.3(4)	49.6(5)	C3–C2–C5	113(1)	115(2)
Ni2–Ni1–Cl1	123.4(2)	122.4(2)	C3–C2–C4	106(1)	108(2)
Ni2–Ni1–P1	120.1(2)	121.9(2)	C2–C5–C10	125(1)	122(2)
Ni1–Ni2–C6	51.4(4)	51.5(4)	C2–C5–C6	112(1)	114(2)
Ni1–Ni2–C1	52.6(4)	51.7(5)	C6–C5–C10	124(2)	124(2)
Ni1–Ni2–P3	113.1(2)	115.0(2)	C5–C6–C7	114(1)	116(2)
Ni1–Ni2–P2	130.9(2)	131.7(2)	Ni2–C6–C7	128(1)	128(1)
C1–Ni2–C6	74.2(6)	73.8(7)	Ni1–C6–C7	126(1)	125(1)
P3–Ni2–C6	96.9(4)	96.0(5)	C6–C7–C8	122(2)	120(2)
P3–Ni2–C1	165.8(5)	166.5(5)	C7–C8–C9	122(2)	121(2)
P2–Ni2–C6	158.2(4)	158.7(5)	C8–C9–C10	120(2)	122(2)
P2–Ni2–C1	91.5(5)	93.2(5)			

structural characteristics of 3 closely resemble those already described for the bimetallic subunits of 2, although there are some noteworthy features which merit some comment. As in the parent compound, there is a short Ni–Ni separation (2.393(3) Å; 2.384(3) Å in 2) suggestive of a strong M–M bonding interaction. The organic $CHCMe_2$-*o*-C_6H_4 chain also behaves as a bidentate ligand through the alkylidene and aryl functionalities, but while the alkylidene end symmetrically bridges the two Ni atoms (Ni(1)–C(1) = 1.95(1); Ni(2)–C(1) = 1.92(1) Å), the Ni(2)–C(6) separation of the aryl carbon at 2.17(1) Å is appreciably longer than the Ni(1)–C(6) bond length of 1.99(2) Å. This is in keeping with the nonsymmetric nature of this compound and with its consideration, in a formal sense, as a Ni(II)–Ni(0) bimetallic species (see Discussion).

Complex 3 is a fluxional molecule in solution. At 20 °C, its $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets in a 2:1 ratio, with the less intense signal being significantly broad. Broad absorptions are also discerned for the ^1H and ^{13}C resonances of the μ-CHR group, although chemical shift values are very similar to those found for 2 (δ_H 4.54, br t, $^3J_{HP}$ = 10 Hz; δ_C 137.5, br s). It is clear that, at ambient temperature, a fast exchange process involving the unique PMe_3 ligand is taking place. This process is probably dissociative, thus explaining our failure to observe ^{13}C–^{31}P coupling between the M–*C*HR carbon and the transoid PMe_3 ligand, and since it time-averages the two Ni moieties, it might involve the formation of a symmetric, chloride-bridged intermediate species.

Addition of the chelating diphosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) to solutions of 2 induces cleavage of the chloride bridges and affords the related bimetallic alkylidene derivative 4 as well (eq 3). Complex 4 is also a dark red material, very air sensitive both in solution and in the solid state. As expected for the proposed formulation, it exhibits poor solubility in hydrocarbon solvents, although it is soluble in CH_2Cl_2. Solutions of 4 are thermally unstable and decompose slowly upon standing at room temperature, even under an inert atmosphere. For this reason accurate analytical data for 4 have proved unattainable, but the compound has been fully characterized by NMR methods. It should be mentioned, in addition, that its spectroscopic properties are very similar to those reported for the related and structurally characterized[4c] diplatinum species $[Pt_2(\mu\text{-}CHCH_2Ph)(\mu\text{-}H)(diphos)_2]BF_4$ (diphos = $Ph_2PCH_2CH_2PPh_2$). Thus, the symmetrical structure proposed for 4 is in agreement with the observation of an AX spin system for the ^{31}P nuclei of the chelating dmpe ligands (δ_A 20.6, δ_X 35.0 ppm, $^2J_{AX}$ = 7.5 Hz), while on the other hand a triplet of triplets is observed in both the ^1H (δ 4.6, $^3J_{HP}$ = 14.4 and 1.5 Hz) and the ^{13}C NMR spectra (δ 126.9, $^2J_{CP}$ = 53 and 8 Hz) for the ^1H and ^{13}C atoms of the alkylidene functionality.[25]



(3)

The novel alkylidene-bridged complex $CpNi(\mu_2\text{-}CHCMe_2\text{-}o\text{-}C_6H_4)Ni(PMe_3)_2$ (5) can be obtained from the reaction of 2 with NaCp (eq 4). Compound 5 is a dark red crystalline solid, soluble in most common organic solvents, for which analytical and spectroscopic data are in accord

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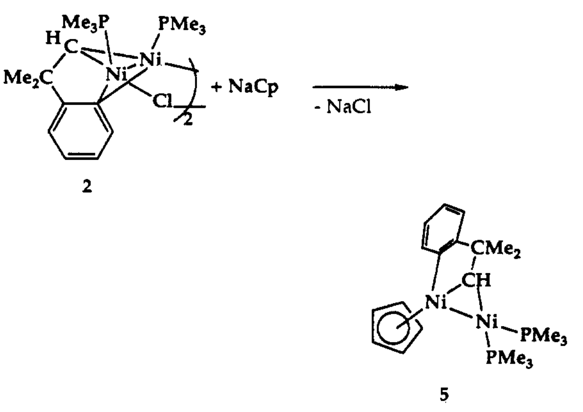
[25] By analogy with 2, for which there is only one J_{HP} coupling which is clearly cisoid, the larger coupling is attributed to the cisoid H–P interaction with the smaller due to the transoid coupling. The ^{13}C–^{31}P couplings are normal, however, the transoid coupling being larger than the cisoid.



(4)

with the proposed formulation. The most interesting NMR features of 5 are those pertaining to the Ni$_2$(μ-CHR) entity. The alkylidene proton appears at δ 7.0 as a doublet of doublets ($^3J_{HP}$ = 6.6 and 2.4 Hz) due to its coupling to two nonequivalent PMe$_3$ ligands, while the ^{13}C{^{1}H} NMR spectrum shows its supporting carbon resonating at 161.4 ppm, with only one resolvable coupling, namely that due to the transoid phosphorus, $^2J_{CP}$ = 43 Hz ($^1J_{CH}$ = 129 Hz). These ^{1}H and ^{13}C chemical shifts are within the range expected for alkylidene ligands acting as bridges between two metal centers.[2a,c] The nickel-bonded quaternary aromatic carbon appears as a singlet at 147.3 ppm, and this clearly demonstrates that, at variance with the situation found in compound 2, this carbon is not bridging the two metal atoms but is instead bound to only one Ni center, that bearing no PMe$_3$ ligands. Complex 5 exhibits good thermal stability, being indefinitely stable at room temperature when kept under an inert atmosphere. At variance with 2, it does not react with PMe$_3$, even under rather forcing conditions (20 equiv net PMe$_3$, 60 °C, 12 h).

The simple synthetic methodology described above can be applied to the preparation of analogs of 5 having a substituted cyclopentadienyl ligand. Thus, treatment of 2 with NaC$_5$H$_4$R (R = Me, *i*-Pr) affords the expected derivatives 6 (R = Me) and 7 (R = *i*-Pr). The new compounds are also dark red, air-sensitive crystalline materials, displaying physical properties analogous to those of 5. Spectroscopic features are also alike (see Experimental Section) and merit no further comments.

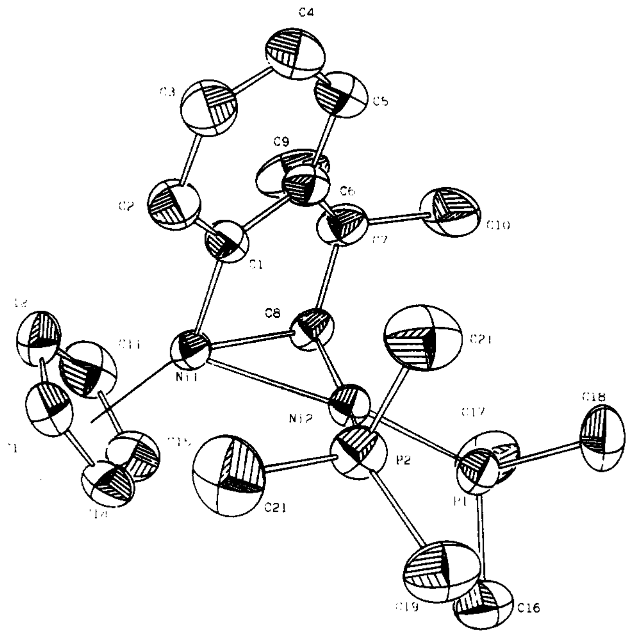


Figure 4. ORTEP representation for 5 showing the thermal ellipsoids at 50% probability and giving the atom-labeling scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) for 5

Ni1–Ni2	2.353(1)	P2–C21	1.805(6)
Ni1–C1	1.880(4)	C1–C2	1.407(6)
Ni1–C8	1.904(4)	C1–C6	1.399(6)
Ni1–C12	2.130(5)	C2–C3	1.400(6)
Ni1–C11	2.124(6)	C3–C4	1.376(7)
Ni1–C13	2.154(5)	C4–C5	1.382(7)
Ni1–C14	2.156(5)	C5–C6	1.388(6)
Ni1–C15	2.113(3)	C6–C7	1.508(6)
Ni2–P1	2.134(1)	C7–C8	1.541(6)
Ni2–P2	2.210(1)	C7–C9	1.535(7)
Ni2–C8	1.867(4)	C7–C10	1.527(7)
P1–C16	1.812(5)	C11–C12	1.406(8)
P1–C17	1.817(6)	C11–C15	1.423(8)
P1–C18	1.806(6)	C12–C13	1.403(8)
P2–C19	1.817(6)	C13–C14	1.392(7)
P2–C20	1.805(6)	C14–C15	1.407(7)
C1–Ni1–C8	84.0(2)	C19–P2–C20	99.5(3)
Ni2–Ni1–C8	50.7(1)	Ni1–C1–C6	115.6(3)
Ni2–Ni1–C1	80.1(1)	Ni1–C1–C2	125.6(3)
Ni1–Ni2–C8	52.1(1)	C2–C1–C6	118.7(4)
Ni1–Ni2–P2	110.14(6)	C1–C2–C3	119.9(4)
Ni1–Ni2–P1	142.87(7)	C2–C3–C4	120.4(5)
P2–Ni2–C8	154.9(1)	C3–C4–C5	120.1(4)
P1–Ni2–C8	99.6(1)	C4–C5–C6	120.4(4)
P1–Ni2–P2	103.35(6)	C1–C6–C5	120.4(4)
Ni2–P1–C18	118.9(2)	C5–C6–C7	125.3(4)
Ni2–P1–C17	118.4(2)	C1–C6–C7	114.2(4)
Ni2–P1–C16	114.0(2)	C6–C7–C10	113.0(4)
C17–P1–C18	101.6(3)	C6–C7–C9	108.9(4)
C16–P1–C18	101.8(3)	C6–C7–C8	104.6(4)
C16–P1–C17	99.0(3)	C9–C7–C10	107.8(4)
Ni2–P2–C21	106.8(2)	C8–C7–C10	112.6(4)
Ni2–P2–C20	119.4(2)	C8–C7–C9	109.9(4)
Ni2–P2–C19	124.1(2)	Ni2–C8–C7	113.8(3)
C20–P2–C21	102.6(3)	Ni1–C8–C7	111.1(3)
C19–P2–C21	101.3(3)	Ni1–C8–Ni2	77.2(2)

The structure proposed for compounds 5–7 on the basis of analytical and spectroscopic data has been confirmed with the aid of a single-crystal X-ray investigation, carried out with 5. The molecular structure of this complex is illustrated in Figure 4, which also shows the atom-labeling scheme. As can be seen, the molecules consist of two metal–metal-bonded nickel centers, with a short Ni(1)–Ni(2) contact of 2.353(1) Å. This is in fact appreciably smaller than the analogous distance in compounds 2 and 3 (2.384(3) Å in 2; 2.393(3) Å in 3) and, as in these two cases, is indicative of a substantial M–M-bonding interaction. The dimetallacyclopropane structure of 5 is completed by the alkylidene ligand, which unsymmetrically bridges the Ni(1) and Ni(2) fragments. Interestingly, the Ni(1)–C(8) distance at 1.904(4) Å is longer than that associated with the remaining nickel atom, viz. Ni(2)–C(8), of 1.867(4) Å. As for compound 3, this is a rather unusual situation because, with few exceptions, most of the known homobimetallic μ-alkylidene complexes are symmetric.[2c] The internal Ni(1)–C(8)–Ni(2) angle of 77.2(2)° has a standard value for bridging alkylidene structures.[6] Other internuclear distances in 5 are also conventional. For instance, the Ni(1)–C(1) length of 1.880(4) Å compares favorably with typical Ni–aryl bond separations.[26] Finally, it should also be mentioned that the Ni–PMe$_3$ bond of 2.210(1) Å to the phosphine group transoid to the alkylidene ligand (C(8)–Ni(2)–P(2) = 154.9(1)°) is appreciably longer than the Ni(2)–P(1) separation at 2.134-

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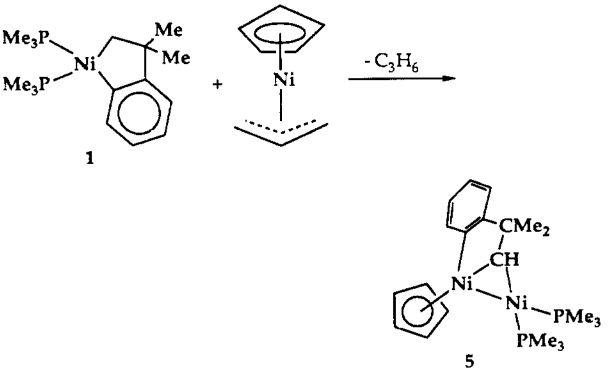
(26) (a) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1969**, 266. (b) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987**, *334*, 141.

(1) Å. This may be due to the higher trans influence of the carbenoid unit.

As already mentioned, in the synthesis of complex **2** the η^3-*o*-xylyl complex not only captures a PMe_3 ligand from **1** but also, and more importantly, removes one of the H atoms of the Ni-bound methylene group, giving rise to the alkylidene functionality. In order to ascertain the scope of this unusual reaction, and its applicability to other related systems, we have used the 18-electron allyl $CpNi(\eta^3\text{-}C_3H_5)$ as the H-abstracting reagent as, in a favorable case, the formation of **5** is to be expected.

Mixing benzene solutions of **1** and $CpNi(\eta^3\text{-}C_3H_5)$, at room temperature, results in no reaction, although an interesting observation was effected upon analyzing the mixture by $^{13}C\{^1H\}$ NMR spectroscopy. Complex **1** is known to be a highly fluxional molecule that, at 20 °C, undergoes a fast PMe_3 exchange with traces of PMe_3 present in solution,[9] this process being only partially suppressed at temperatures of about −80 °C. Rather astonishingly, the $^{13}C\{^1H\}$ NMR of mixtures of **1** and $CpNi(\eta^3\text{-}C_3H_5)$ is comparable with that of pure **1** recorded at −80 °C. Therefore, the allyl complex acts as a very effective PMe_3 trapping reagent and this results in a considerable decrease of the PMe_3 exchange rate. To confirm this, $CpNi(\eta^3\text{-}C_3H_5)$ was reacted with an excess of PMe_3, reductive elimination accompanied by formation of $Ni(PMe_3)_4$ being observed. Similar reactivity has been reported for other PR_3 ligands,[27] but the reaction with PMe_3 is particularly fast.

When the mixtures of $CpNi(\eta^3\text{-}C_3H_5)$ and **1** are heated to 60 °C, a reaction proceeds, but NMR monitoring indicates the formation of a number of Cp-containing products, along with $Ni(PMe_3)_4$. However, if the reaction is performed in a way such that the allyl complex is always present in a large excess, i.e. by slow addition of solutions of **1** to those of $CpNi(\eta^3\text{-}C_3H_5)$, both maintained at 60 °C, reductive elimination to Ni(0) is minimized and the expected product **5** is formed (eq 5) in a very selective manner (70% yield based on a Cp balance). Once again, α-H abstraction by a Ni–allyl fragment occurs, this time with liberation of C_3H_6, followed by coupling of the resulting fragments and ligand reorganization.

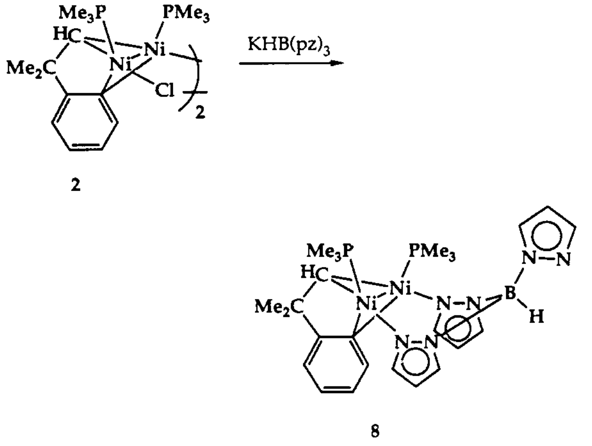


1

5

(5)

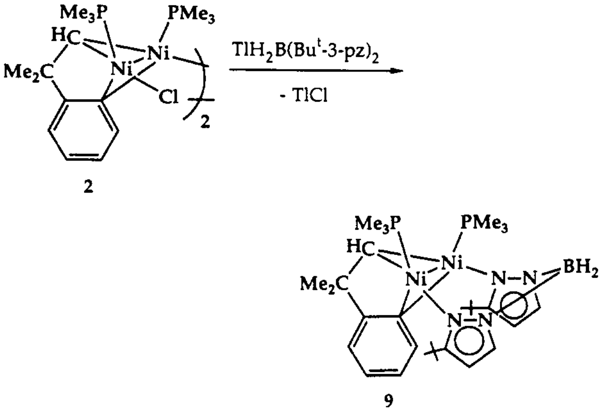
In recent years there has been much renewed interest in transition-metal compounds of the poly(pyrazolyl)borate ligands. Within this family of substances, the tris(pyrazolyl)borate group ($HB(pz)_3$, Tp, from now onward) has been shown in many instances to behave similarly to the ubiquitous cyclopentadienyl group, although important differences in their chemical behavior have also been noticed.[28] We have considered of interest the synthesis of alkylidene complexes of nickel, related to **5**–**7**, but containing a Tp ligand instead of a cyclopentadienyl, and with this objective in mind we have performed the reaction of **2** with KTp. Red crystals of the new alkylidene complex **8** can be readily isolated from the reaction mixture, but spectroscopic data do not conform with a nonsymmetric formulation of the type described above for **5**–**7**. For example, the $^{31}P\{^1H\}$ NMR spectrum shows equivalent PMe_3 ligands, and in addition the two ^{31}P nuclei couple equally with both the alkylidene carbon (δ_C = 111.4 t, $^2J_{CP}$ = 9 Hz, $^1J_{CH}$ = 132 Hz) and the Ni-bound arylic carbon (δ_C = 140 t, $^2J_{CP}$ = 40 Hz). These observations suggest that formation of **8** proceeds as indicated in eq 6, that is, that the Tp group is not acting as a tridentate, formally five-electron donor but is instead employing two of the pyrazolyl rings to bridge the two nickel centers. The existence of a noncoordinated pyrazolyl arm in **8** is also supported by the spectroscopic similarity of **8** with the new compound **9**, which, as shown in eq 7, is the product of the reaction of **2** with the thalium salt of the bis(pyrazolyl)borate ligand $H_2B(3\text{-}t\text{-}Bu\text{-}pz)_2$.



2

8

(6)



2

9

(7)

Discussion

Complex **2** is an unexpected product of the reaction of $NiCl_2(PMe_3)_2$ with $Mg(CH_2CMe_2Ph)Cl$. It is in fact the first non-heteroatom-stabilized alkylidene complex of nickel. Mononuclear, heteroatom-stabilized alkylidene complexes of Ni are known,[2,29,30] but analogous homo- and

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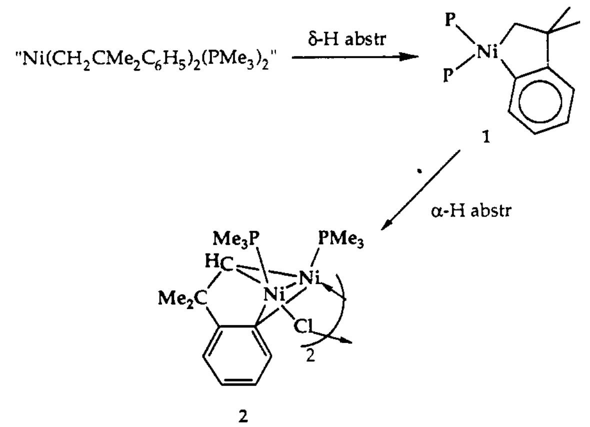
(27) Harder, V.; Werner, H. *Helv. Chim. Acta* **1973**, *56*, 549.

(28) (a) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (b) Shaver, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 245. (c) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(29) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583 and references therein.

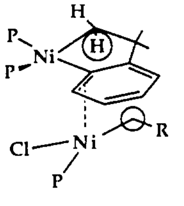
Scheme II



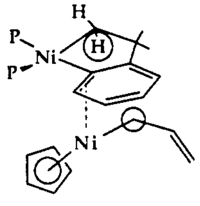
heterobinuclear derivatives are infrequent.[31] The formation of the transient $\mathrm{Cp(L)Ni{=}CH_2^+}$ (L = P-donor ligand) has been postulated in some methylene transfer reactions,[32a] and naked $\mathrm{Ni{=}CH_2}$ and $\mathrm{N_2Ni{=}CH_2}$ have been synthesized in Ar matrices and characterized by matrix isolation spectroscopy.[32b] Methylene-bridged M—Ni (M = Mo, W) and Ta—Ni complexes have been reported recently.[23b,c,33]

The stepwise formation of **2**, starting from the unstable dialkyl "$\mathrm{Ni(CH_2CMe_2Ph)_2(PMe_3)_2}$", can be represented as depicted in Scheme II. Thus, one of the original neophyl ligands undergoes a double H-abstraction: first an intramolecular δ-H elimination from the dialkyl to afford the metallacycle **1** and then an intermolecular α-H abstraction induced by an unsaturated organometallic species. The latter process exemplifies an uncommon type of reactivity for metallacyclic units[8] and represents, to our knowledge, the first reported example of an α-elimination reaction from a metallacycle to yield an isolable alkylidene complex. Apart from carbyne formation, multiple H-abstractions from metal-bound organic fragments are rare, although some examples have been described in the literature.[34]

As α-C–H abstracting reagents, other 16-electron nickel organometallic compounds can be used in place of the *o*-xylyl derivative and, in fact, an alkylidene complex analogous to **2**, containing bromide bridging ligands, can be obtained by reacting **1** with $\mathrm{[NiBr(\eta^3\text{-}C_3H_5)]_2}$. Even some Ni–chloroalkyls can effect this transformation, but the reactions are not so well behaved, require heating at 50–60 °C, and provide only small quantities of **2**. This may explain the very low yields of this compound in the reaction leading to **1**. Also, and as shown in Results, even some 18-electron Ni allyls such as $\mathrm{CpNi(\eta^3\text{-}C_3H_5)}$ can be used as reagents in this α-C–H abstraction, in this case to afford the alkylidene **5**. Interestingly, and at variance with the results found for the Ni complex $\mathrm{CpNi(\eta^3\text{-}C_3H_5)}$, the very strong $\mathrm{PMe_3}$ trapping reagent $\mathrm{CpPd(\eta^3\text{-}C_3H_5)}$ does not produce a related alkylidene complex. Curiously enough, although slightly out of context, the addition of this species to solutions of **1** completely suppresses the phosphine exchange phenomenon distinctive of solutions of the nickelacycle, so that this molecule behaves as rigid even at room temperature.[35] This clearly demonstrates that the formation of **2** or **5** does not imply an intramolecular dissociation of $\mathrm{PMe_3}$ from **1** but instead a bimolecular process involving, as active intermediates, species of type **A** or **B**. The electron-rich nature of the aromatic ring in **1** facilities its incorporation into the coordination sphere of the incoming Ni center,[36] and for the formation of **2**, this can be followed by binuclear coupling elimination of *o*-xylene to afford **3**. The latter compound is known to lose $\mathrm{PMe_3}$ in solution (vide supra) to produce a mixture of **2** and the ylide $\overline{\mathrm{Ni[C(H)(PMe_3)CMe_2C}}\mathrm{_6H_4]Cl(PMe_3)}$,[24] this last species resulting from the reaction of still-unaltered **3** with $\mathrm{PMe_3}$. Thus, the second equivalent of the η^3-*o*-xylyl derivative used in the synthesis of **2** not only makes extrusion of $\mathrm{PMe_3}$ from **3** easier but also avoids the formation of the aforementioned ylide by preferentially trapping the dissociated $\mathrm{PMe_3}$.



A



B

Some brief comments should also be devoted to the mechanistic pathway leading to **5**. Similar to the formation of **2**, an intermediate of type **B**, in which the close proximity of the Ni centers facilitates the bimetallic reductive elimination, can be reasonably proposed. As already pointed out, $\mathrm{CpNi(\eta^3\text{-}C_3H_5)}$ reacts readily with $\mathrm{PMe_3}$, probably through an η^1-allyl intermediate. In our system, the electron-rich aromatic ring of **1** may act as a two-electron donor although, perhaps due to steric and electronic effects, this kind of intermediate **B** becomes accessible only at moderately high temperatures. In connection with this, it should be mentioned that arenes can bind Ni(II) centers[37] and that there is plentiful precedent for CpNi(R)(olefin)[38] complexes.

The bonding characteristics of bridging alkylidenes have been extensively studied.[39] Two limiting structures are usually considered for this type of compound, and this

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(30) See for example: (a) Miller, J.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069. (b) Wada, M.; Asada, N.; Oguro, K. *Inorg. Chem.* **1978**, *17*, 2353. (c) Wada, M.; Sameshima, K.; Nishiwaki, K.; Kawasaki, Y. *J. Chem. Soc., Dalton Trans.* **1982**, 793.

(31) (a) Fischer, E. O.; Beck, H. J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72. (b) Berry, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1601. (c) Fontaine, X. L. R.; Huggins, S. J.; Shaw, B. L.; Thornton-Pett, M.; Yichang, W. *J. Chem. Soc., Dalton Trans* **1987**, 150.

(32) (a) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1178. (b) Chang, S.-C.; Hange, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *Inorg. Chem.* **1990**, *29*, 4373.

(33) (a) Chetcuti, M. J.; Fanwick, P. E.; Grant, B. E. *Organometallics* **1991**, *10*, 3003. (b) Chetcuti, M. J.; Deck, K. J.; Gordon, J. C.; Grant, B. E. *Organometallics* **1992**, *11*, 2128.

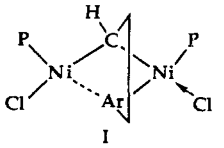
(34) For some recent examples see: (a) Werner, H.; Weber, B.; Nürnberg, O.; Wolf, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1025. (b) Hessen, B.; Spek, A. L.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1058. (c) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.

(35) NMR data of rigid 1 (20 °C, in the presence of 1 equiv of $\mathrm{CpPd(C_3H_5)}$): $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$) δ −26.0 (d, $^2J_{\mathrm{PP}}$ = 23 Hz), −21.3 (d); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$) δ 16.7 (d, $^2J_{\mathrm{CP}}$ = 20 Hz, $\mathrm{PMe_3}$), 18.1 (d, $^2J_{\mathrm{CP}}$ = 17 Hz, $\mathrm{PMe_3}$), 35.8 (d, $^4J_{\mathrm{CP}}$ = 5.8 Hz, C*Me*$_2$), 51.0 (m, *C*Me$_2$), 52.8 (dd, $^2J_{\mathrm{CP}}$ = 95 and 9 Hz, Ni–$\mathrm{CH_2}$), 122.3, 123.4, 123.9 (d, J_{CP} = 4; s; d, J_{CP} = 9 Hz, 3 CH aromatics), 138.3 (m, CH aromatic), 167.4 (s, quaternary aromatic), 169.5 (dd, $^2J_{\mathrm{CP}}$ = 120 and 12 Hz, Ni–$\mathrm{C_{ar}}$).

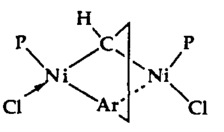
(36) Arene complexes of Ni(II) are known,[37] and η^2 and η^4 coordination of an arene ligand to a transition metal, including nickel, is also well documented: (a) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928. (b) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725. (c) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722. (d) Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273. (e) Benn, R.; Mynott, R.; Topalovic, I.; Scott, F. *Organometallics* **1989**, *8*, 2299 and references therein.

(37) See: Choe, S. B.; Klabunde, K. J. *J. Organomet. Chem.* **1989**, *359*, 409 and references therein.

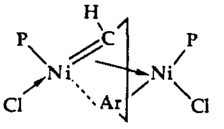
can be represented by means of resonance forms **I–II** and **III–IV**, respectively, in the case of the binuclear subunits present in the molecules of **2**. In **I–II**, two non directly bonded Ni(II) centers are bridged by an sp^3-hybridized carbon and an aryl ligand, while in **III–IV** the formally Ni^0=C< unit[40] acts as an olefin and bonds the second Ni center (formally Ni(II)). Structure **C** is an alternative representation of **III**. In accord with the work of Grubbs,[23a] the dative C→Ni and Ni←Ni interactions in this structure may be respectively regarded as the σ and π components of the synergistic Ni–"olefin" bond. The short Ni–C(1) distances in **2** (ca. 1.90 Å) and the value of the alkylidene carbon chemical shift (120.2 ppm) seem to argue in favor of a larger contribution of resonance structures **III–IV** and hence of formulation of **2** as a compound containing two M–M-bonded Ni(I) centers.



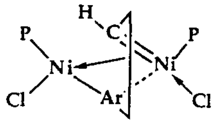
I



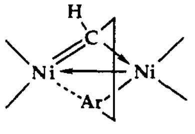
II



III

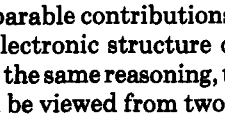


IV

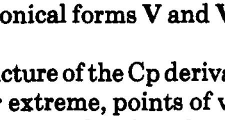


C

Similar considerations apply to the bimetallic alkylidene complex **3**, for which resonance forms of types **V** and **VI** can be readily envisaged. At variance with the situation described above, both **V** and **VI** imply formulation of **3** as a Ni(1)^{II}–Ni(2)^0 species; i.e., Ni(1) is formally in oxidation state II in the two structures, while Ni(2) is Ni(0) also in both. The symmetry of the Ni(CHR)Ni bridge suggests comparable contributions of canonical forms **V** and **VI** to the electronic structure of **3**.



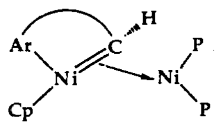
V



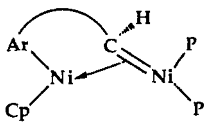
VI

By the same reasoning, the structure of the Cp derivative **5** can be viewed from two, rather extreme, points of view. In the first instance, the complex can be thought of as consisting of a NiP$_2$ fragment coordinated to the nickelaolefin Cp(Ar)Ni=CHR, i.e. to a Ni(II)–alkylidene moiety. In this respect it should be noted that (i) while mononuclear, non-heteroatom-stabilized alkylidene complexes of Ni (either in the II or in the 0 oxidation state) have, so far, avoided isolation, their stabilization by coordination to a suitable metal fragment seems quite feasible and (ii) Ni(0) complexes of olefins[41,42] and η^2-arene[36d,e] ligands have ample literature precedent. In the second alternative, the structure of **5** may be described as consisting of a CpNi(Ar) fragment coordinated to a nickelaolefin of the type C(H)R=NiP$_2$, that is, to a Ni(0)–alkylidene functionality. Heteroatom-stabilized alkylidene complexes of Ni(0) have been isolated recently,[40] and on the other hand, stabilization of a C(H)R=NiP$_2$ group by coordination to an isolobal fragment appears a reasonable possibility. In addition, and as pointed out above, olefin complexes of CpNi(R) fragments have also been described in the literature.

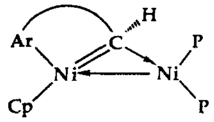
The above limiting structures can be respectively associated with resonance forms **VII** and **VIII**, structure **D** being an alternative representation of canonical form **VII**. Once again, the dative C→Ni and Ni←Ni interactions in **D** may be respectively regarded as the σ and π components of the synergic Ni–"olefin" bond. As for **2**, both resonance forms imply formulation of the compound as containing a Ni(II) and a Ni(0) fragment. Hence, **5** should also be viewed as a mixed-valence species. The nonsymmetric nature of **5** and the failure to observe displacement of the NiP$_2$ fragment upon addition of PMe$_3$ seem to favor a somewhat larger contribution of **VIII** to the overall structure of this compound. Hence, the alkylidene ligand seems to prefer coordination to a Ni(0) center rather than an 18e$^-$ Ni(II) configuration.



VII



VIII



D

Lastly, in the case of the poly(pyrazolyl)borate derivatives **8** and **9**, their symmetric nature resembles that previously found for **2**. Hence, similar electronic structures (**IX** and **X**) can be proposed to account for their electronic properties. These correspond in fact to formulation of **8** and **9** as species containing two metal–metal-bonded Ni(I) centers.

Some comments must be devoted to the NMR characteristics of the μ_2-CHR moiety in the Ni dimeric entities. Proton chemical shifts for bridging alkylidene ligands have been found in the range 4–11 ppm, although they usually

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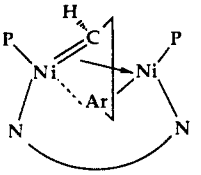
(38) See for example: (a) Lehmkuhl, H.; Keil, T. *J. Organomet. Chem.* **1988**, *342*, C38. (b) Lehmkuhl, H.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G. *Chem. Ber.* **1986**, *119*, 2542. (c) Lehmkuhl, H.; Naydowski, C.; Danowski, F.; Bellenbaum, M.; Benn, R.; Rufinska, A.; Schroth, G.; Mynott, R.; Pasynkiewicz, S. *Chem. Ber.* **1984**, *117*, 3231. (d) Lehmkuhl, H.; Keil, T.; Benn, R.; Rufinska, A.; Krüger, C.; Poplawska, J.; Bellenbaum, M. *Chem. Ber.* **1988**, *121*, 1931.

(39) See ref 2a,c and references therein.

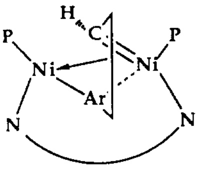
(40) In contrast to the large number of Fischer-type alkylidene complexes of Ni(II) that have been known for many years,[2a] the analogous Ni(0) derivatives have been characterized only very recently. See: Gabor, B.; Krüger, C.; Marczinke, B.; Mynott, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666.

(41) (a) Fischer, K.; Jonas, K.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 565. (b) Kaschube, W.; Pörschke, K. R.; Bonrath, W.; Krüger, C.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 772. (c) Bonrath, W.; Pörschke, K. R.; Michaelis, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 298. (d) Kaschube, W.; Schröder, W.; Pörschke, K. R.; Angermund, K.; Krüger, C. *J. Organomet. Chem.* **1990**, *389*, 399.

(42) (a) Pörschke, K. R.; Jonas, K.; Wilke, G.; Benn, R.; Mynott, R.; Goddard, R.; Krüger, C. *Chem. Ber.* **1985**, *118*, 275 and three following papers in this volume. (b) Pörschke, K. R.; Jonas, K.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1913. (c) Kaschube, W.; Pörschke, K. R.; Angermund, K.; Krüger, C.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1921.



IX



X

cluster around 6–11 ppm.[2c,33] Therefore, the ^{1}H resonance of the alkylidene ligand in complexes **8** and **9** (ca. δ 2.73), also in **2** (δ 3.45), and to a lesser extent in **3** and **4** (ca. δ 4.6) is remarkably at high field; i.e., some of them are becoming close to the domain characteristic of non-metal-bonded μ-alkylidene functionalities.[2] Since the alkylidene carbon resonances in these complexes have normal values (120.2, 137.5, 126.9, 111, and 108 ppm for **2**, **3**, **4**, **8**, and **9**, respectively), it seems that other subtle factors may be responsible for this, apparently abnormal, ^{1}H shift. In fact, we note that in the more electron-rich Cp derivatives such as **5** the μ_2-CHR proton resonates at ca. 7 ppm. It seems likely that the geometrical location of this proton between the two phosphine ligands (see Figure 2) may be the cause of this strong shielding effect. From these observations it can be concluded that the use of δ(C*H*R) to establish the existence of a M–M bond in M(μ-CHR)M complexes may be misleading, while ^{13}C chemical shift values are more reliable and reflect the presence of a M–M-bonding interaction.

In conclusion, we have convincingly demonstrated that allylic or pseudoallylic complexes of nickel can be used as α-H abstracting reagents for the generation of unusual alkylidene-bridged complexes, in their reaction with the nickelacycle **1**. This is a new type of reactivity for metallacyclic units and leads, in the present case, to isolable, stable di- and tetrametallic alkylidene compounds.

Experimental Section

Microanalyses were performed by Pascher Microanalytical Laboratory, Remagen, Germany, and the Microanalytical Service of the University of Sevilla. Perkin-Elmer Model 577 and 684 spectrometers were used for IR spectra, and a Varian XL-200 instrument was used for NMR studies. The ^{13}C resonance of the solvent was used as internal reference, but chemical shifts are reported with respect to SiMe$_4$. ^{31}P NMR shifts are relative to external 85% H$_3$PO$_4$. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The compounds $\overline{\text{Ni(CH}_2\text{CMe}_2\text{-}o\text{-C}}_6H_4$)(PMe$_3$)$_2$,[9] Ni($\eta^3$-CH$_2C_6H_4$-*o*-Me)Cl(PMe$_3$),[13] [Ni(C$_5H_5$)($\eta^3$-C$_3H_5$)],[43] K[HB(pz)$_3$][44] and Tl-[H$_2$B(3-*t*-Bu-pz)$_2$][45] were obtained by published methods.

Synthesis of the Alkylidene-Bridged Complex 2. Toluene solutions of $\overline{\text{Ni(CH}_2\text{CMe}_2\text{-}o\text{-C}}_6H_4$)(PMe$_3$)$_2$ (1.7 g, 5 mmol; 40 mL) and Ni(η^3-CH$_2$C$_6$H$_4$-*o*-Me)Cl(PMe$_3$) (2.75 g, 10 mmol; 50 mL) were mixed, without stirring. The appearance of a dark crystalline precipitate was noted, and the mixture was left undisturbed for 3 days at room temperature. Complex **2** was then filtered, washed with Et$_2$O (3 × 20 mL), and dried in vacuo (yield: 80–90%). The mother liquor was evaporated to dryness, the residue was extracted with 70 mL of Et$_2$O and the extract was filtered. Concentration and cooling furnished the known compound Ni(η^1-CH$_2$C$_6$H$_4$-*o*-Me)Cl(PMe$_3$)$_2$ as yellow crystals (several crops, 90% yield). ^{1}H NMR (CD$_3$CN): δ 1.35 (d, 18 H, $^2J_{\mathrm{HP}}$ = 8.3 Hz, 2 PMe$_3$), 1.41 (s, 6 H, CMe$_2$), 3.45 (t, 1 H, $^3J_{\mathrm{HP}}$ = 14.3 Hz, Ni$_2$CH), 6.8–7.8 (m, 4 H, aromatics). ^{31}P{^{1}H} NMR (CD$_3$CN): δ −9.2 s. ^{13}C{^{1}H} NMR: δ 15.1 (d, $^1J_{\mathrm{CP}}$ = 26 Hz, PMe$_3$), 34.9 (s, C*Me*$_2$), 57.2 (s, *C*Me$_2$), 120.2 (br s, Ni$_2$CH), 120.5 123.2, 128.7, 153.2 (s, CH aromatics), 165.7 (s, quaternary aromatic). The bridging C$_{\mathrm{ar}}$ atom was not located. Anal. Calcd for **2**·$^1/_6$C$_6$H$_6$: C, 45.4; H, 6.7. Found: C, 45.4; H, 6.8. The analytical sample was synthesized in C$_6$H$_6$. The presence of this solvent in the crystalline material obtained was ascertained by ^{1}H and ^{13}C NMR spectroscopy.

Synthesis of Complex 2. Complex **2** (0.3 g, 0.35 mmol) was dissolved in 20 mL of CH$_3$CN, and 0.07 mL (0.7 mmol) of PMe$_3$ was added at room temperature. The resulting mixture was stirred for 20 min and taken to dryness. The residue was extracted with Et$_2$O and the suspension filtered. Concentration and cooling at −30 °C gave complex **3** as dark red, almost black, needles (yield: 30–40%). ^{1}H NMR (C$_6$D$_6$): δ 1.01 (br d, 27 H, J_{HP}(app) = 6.5 Hz, 3 PMe$_3$), 1.56 (s, 6 H, CMe$_2$), 4.54 (br t, 1 H, $^3J_{\mathrm{HP}} \approx$ 10 Hz, Ni$_2$CH), 6.9–8.5 (m, 4 H, aromatics). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −23.9 (br s, 1 P), −16.5 (s, 2 P). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 16.9 (br, PMe$_3$), 34.6 (s, C*Me*$_2$), 58.2 (s, *C*Me$_2$), 120.6, 123.7, 128.4, 151.2 (s, CH aromatics), 137.5 (br s, $^1J_{\mathrm{CH}}$ = 133 Hz, Ni$_2$-CH), 165.1 (s, quaternary aromatic). The bridging C$_{\mathrm{ar}}$ was not located. Anal. Calcd for **3**: C, 44.5; H, 7.4. Found: C, 44.5; H, 7.6.

Synthesis of Complex 4. To a solution of complex **2** (0.1 g, 0.12 mmol) in CH$_3$CN (10 mL) was added an excess of dmpe (0.1 mL, ca. 0.5 mmol) at room temperature. After the mixture was stirred for 30 min, when a light red color formed, the solvent was removed under vacuum and the red residue extracted with CH$_2$Cl$_2$ (10 mL). Slow addition of light petroleum ether furnished compound **4** in 70% yield. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.83 (d, 6 H, $^2J_{\mathrm{HP}}$ = 7.0 Hz, 2 PMe), 1.35 (s, 6 H, CMe$_2$), 1.43 (d, 6 H, $^2J_{\mathrm{HP}}$ = 7.2 Hz, 2 PMe), 1.47 (d, 6 H, $^2J_{\mathrm{HP}}$ = 8.5 Hz, 2 PMe), 1.53 (d, 6 H, $^2J_{\mathrm{HP}}$ = 8.9 Hz, 2 PMe), 4.61 (tt, 1 H, $^3J_{\mathrm{HP}}$ = 14.4 and 1.5 Hz, Ni$_2$CH), 6.9–8.0 (m, 4 H, CH aromatics). The P–CH$_2$ protons appear as a broad hump at ca. 1.5 ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 20.6 (d, $^2J_{\mathrm{PP}}$ = 7.5 Hz), 35.0 (d). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 10–40 (complex m, Me and CH$_2$ carbons), 56.3 (s, *C*Me$_2$), 123.4, 123.8, 131.3, 154.7 (s, s, s, and m, 4 CH aromatics), 126.9 (tt, $^2J_{\mathrm{CP}}$ = 53 and 8 Hz, Ni$_2$CH), 160.0 (s, quaternary aromatic). The bridging C$_{\mathrm{ar}}$ was not located.

Synthesis of the Alkylidene-Bridged Complex 5. Method A. To a hot (60 °C) stirred solution of (C$_5$H$_5$)Ni(η^3-C$_3$H$_5$) (0.13 g, ca. 0.8 mmol) in C$_6$H$_6$ (3 mL) was added dropwise a solution of complex **1** (0.25 g, ca 0.75 mmol) in 5 mL of C$_6$H$_6$ maintained at the same temperature (60 °C). After the addition was complete, the volatiles were removed in vacuo and the residue was extracted with petroleum ether. Centrifugation, partial removal of the solvent, and cooling at −30 °C furnished crude complex **5** in 50% yield. Purification was achieved by recrystallization from petroleum ether.

Method B. A 0.43 g (ca 0.5 mmol) portion of complex **2** was suspended in tetrahydrofuran (25 mL) at room temperature and treated with 2.3 mL of a 0.45 M solution of NaCp in the THF. After the mixture was stirred for 10 h, the solvent was eliminated under reduced pressure and the residue extracted with petroleum ether. Concentration and cooling gave complex **5** as dark red crystals in ca. 65% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.73 (d, 9 H, $^2J_{\mathrm{HP}}$ = 5.9 Hz, PMe$_3$), 0.83 (d, 9 H, $^2J_{\mathrm{HP}}$ = 7.4 Hz, PMe$_3$), 1.49 (s, 3 H, C–Me), 1.65 (s, 3 H, C–Me), 5.51 (s, 5 H, C$_5$H$_5$), 7.02 (dd, 1 H, $^3J_{\mathrm{HP}}$ = 6.6 and 2.4 Hz, Ni$_2$CH), 6.7–7.4 (m, 4 H, aromatics). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −23.9 (d, $^2J_{\mathrm{P_AP_X}}$ = 31 Hz, P$_A$), −17.7 (d, P$_X$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.9 (d, $^1J_{\mathrm{CP}}$ = 19 Hz, PMe$_3$), 18.6 (dd, $^1J_{\mathrm{CP}}$ = 22, $^3J_{\mathrm{CP}}$ = 5 Hz, PMe$_3$), 30.5 (dd, $^4J_{\mathrm{CP}}$ = 8 and 3 Hz, C–*Me*), 36.9 (d, $^4J_{\mathrm{CP}}$ = 9 Hz, C–*Me*), 59.8 (s, *C*Me$_2$), 90.2 (s, C$_5$H$_5$), 119.6, 122.1, 124.3, 144.3 (s, CH aromatics), 147.3 (s, Ni–C$_{\mathrm{ar}}$), 161.4 (d, $^2J_{\mathrm{CP}}$ = 43, $^1J_{\mathrm{CH}}$ = 130 Hz, Ni$_2$CH), 165.3 (s, quaternary aromatic).

By reaction of complex **2** with the appropriate NaC$_5$H$_4$R salts the compounds [(C$_5$H$_4$R)$\overline{\text{Ni}(\mu_2\text{-CHCMe}_2\text{-}o\text{-C}}_6H_4$)Ni(PMe$_3$)$_2$] (R = Me, **6**; R = *i*-Pr, **7**) were similarly obtained in 50–60% yield. Spectroscopic data for **6**: ^{1}H NMR (C$_6$D$_6$) δ 0.72 (d, 9 H, $^2J_{\mathrm{HP}}$ = 5.8 Hz, PMe$_3$), 0.84 (d, 9 H, $^2J_{\mathrm{HP}}$ = 7.3 Hz, PMe$_3$), 1.52 (s, 3 H, C–Me), 1.66 (s, 3 H, C–Me), 2.04 (s, 3 H, C$_5$H$_4$*Me*), 5.1–5.6 (m,

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[43] Fischer, E. O.; Bürger, G. *Chem. Ber.* **1964**, *94*, 2409.
[44] Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.
[45] Trofimenko, S.; Calabrese, J. C.; Thompsoh, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

Table IV. Crystal and Refinement Data for 2, 3, and 5

	2	3	5
formula	$C_{32}H_{58}P_4Cl_2Ni_4$	$C_{19}H_{38}P_3ClNi_2$	$C_{21}H_{34}P_2Ni_2$
M_r	872.44	512.3	465.8
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$
a, Å	9.815(4)	17.152(4)	9.013(2)
b, Å	10.550(4)	18.431(3)	16.675(2)
c, Å	19.669(7)	32.577(5)	15.291(7)
β, deg	104.39(3)		91.04(3)
V, Å^3	1973(1)	10 298(3)	2298(1)
Z	2	16	4
F(000)	912	4320	984
ρ(calcd), g cm^{-3}	1.47	1.32	1.35
temp, °C	22	21	22
μ, cm^{-1}	22.08	17.6	17.87
cryst dimens, mm	0.4 × 0.2 × 0.2	0.4 × 0.4 × 0.3	0.15 × 0.15 × 0.30
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochrom Mo K*α* (λ = 0.710 69 Å)	graphite-monochrom Mo K*α* (λ = 0.710 69 Å)	graphite-monochrom Mo K*α* (λ = 0.710 69 Å)
scan technique	Ω/2*θ*	Ω/2*θ*	Ω/2*θ*
data collected	(−12,0,0) to (12,13,14)	(000) to (20,21,38)	(−12,0,0) to (12,23,21)
no. of unique data	4088	9185	3982
no. of obsd data ($I \geq 2\sigma(I)$)	1767	2873	2652
R(int), %	3.9		0.8
no. of std rflns	3/150	3/207	3/159
decay	≤4% variation	≤5% variation	≤2% variation
R_F, %	8.8	6.3	3.0
$R(\mathrm{w})_F$ (unit weights)	10.0	6.7	3.2
av shift/error	0.09	0.11	0.06

Table V. Final Fractional Coordinates for 2

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å^2
Ni1	0.4566(2)	0.5724(2)	0.3852(1)	331(8)
Ni2	0.6883(2)	0.5769(2)	0.4604(1)	333(8)
Cl	0.2717(5)	0.4966(5)	0.4263(2)	486(18)
P1	0.3339(5)	0.7303(5)	0.3301(3)	460(19)
C11	0.2605(44)	0.8240(34)	0.3808(18)	1637(202)
C12	0.3922(44)	0.8269(38)	0.2723(21)	1640(219)
C13	0.1856(41)	0.6960(36)	0.2714(22)	1546(178)
P2	0.8345(5)	0.7336(5)	0.4917(3)	433(18)
C21	0.8009(43)	0.8248(37)	0.5579(19)	1461(192)
C22	0.8620(38)	0.8469(30)	0.4299(18)	1208(166)
C23	1.0097(31)	0.6884(35)	0.5298(21)	1335(171)
C1	0.6275(17)	0.6231(16)	0.3654(10)	338(60)
C2	0.6727(20)	0.5288(18)	0.3193(10)	414(69)
C3	0.8284(23)	0.5415(24)	0.3198(12)	666(99)
C4	0.5835(24)	0.5355(20)	0.2419(10)	574(87)
C5	0.6443(18)	0.4028(17)	0.3530(9)	368(64)
C6	0.5857(18)	0.4191(18)	0.4112(9)	380(62)
C7	0.5597(20)	0.3077(16)	0.4433(10)	408(70)
C8	0.5829(23)	0.1907(16)	0.4204(12)	486(74)
C9	0.6414(26)	0.1791(21)	0.3639(13)	605(96)
C10	0.6737(22)	0.2833(21)	0.3315(11)	521(85)

[a] $U_{eq} = {}^1/_3\sum[U_{ij}a_i{}^*a_j{}^*a_ia_j\cos(\mathbf{a}_i\cdot\mathbf{a}_j)] \times 10^4$.

4 H, C_5H_4Me), 6.92 (dd, 1 H, $^3J_{HP}$ = 6.5 and 2.2 Hz, Ni_2CH), 6.7–7.4 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.8 (d, $^2J_{P_AP_X}$ = 32 Hz, P_A), −17.7 (d, P_X); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 13.9 (s, C_5H_4Me), 16.8 (d, $^1J_{CP}$ = 19 Hz, PMe_3), 18.7 (dd, $^1J_{CP}$ = 22, $^3J_{CP}$ = 5 Hz, PMe_3), 30.4 (d, $^4J_{CP}$ = 8 Hz, C–*Me*), 36.8 (d, $^4J_{CP}$ = 9 Hz, C–*Me*), 59.5 (s, CMe_2), 87.9, 90.2, 91.8 (s, 1:1:2 ratio, CH Cp ring), 101.1 (s, *C*–Me Cp ring), 119.4, 121.9, 124.4, 143.3 (s, CH aromatics), 149.7 (s, Ni–C_{ar}), 164.9 (d, $^2J_{CP}$ = 43 Hz, Ni_2CH), 165.8 (s, quaternary aromatic). Anal. Calcd for **6**: C, 55.1; H, 7.5. Found: C, 54.4; H, 7.8. Spectroscopic data for **7**: ^1H NMR (C_6D_6) δ 0.74 (d, 9 H, $^2J_{HP}$ = 5.8 Hz, PMe_3), 0.86 (d, 9 H, $^2J_{HP}$ = 7.2 Hz, PMe_3), 1.27 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*), 1.32 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*), 1.51 (s, 3 H, C–Me), 1.68 (s, 3 H, C–Me), 2.77 (h, 1 H, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$), 5.1–5.7 (m, 4 H, C_5H_4-*i*-Pr), 6.90 (dd, 1 H, $^3J_{HP}$ = 5.7 and 2.2 Hz, Ni_2CH), 6.7–7.4 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −24.0 (d, $^2J_{P_AP_X}$ = 31 Hz, P_A), −12.3 (d, P_X); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 16.9 (d, $^1J_{CP}$ = 17 Hz, PMe_3), 18.8 (dd, $^1J_{CP}$ = 22, $^3J_{CP}$ = 5 Hz, PMe_3), 23.1 (s, CH*Me*), 24.8 (s, CH*Me*), 27.1 (s, $CHMe_2$), 30.5 (d, $^4J_{CP}$ = 5 Hz, C–*Me*), 36.8 (d, $^4J_{CP}$ = 9 Hz, C–*Me*), 59.6 (s, CMe_2), 87.5, 88.3, 89.2, 92.3 (s, 4 CH Cp ring), 113.1 (s, *C*-*i*-Pr Cp ring), 119.5, 122.0, 124.4, 143.3 (s, CH aromatics), 148.9 (s, Ni-C_{ar}), 164.5 (d, $^2J_{CP}$ = 43 Hz, Ni_2CH), 165.6 (s, quaternary aromatic).

Synthesis of the Hydrotris(pyrazolyl)borate Derivative 8. To a suspension of complex **2** (0.23 g, 0.26 mmol) in THF (70 mL) was added a solution of $KHB(pz)_3$ (0.13 g, 0.53 mmol) in THF (10 mL). The mixture was stirred for ca. 15 h. After that time, the solvent was evaporated under vacuum and the residue extracted with petroleum ether. After concentration and cooling at −20 °C, red crystals of compound **8** were obtained (0.15 g, yield 47%). ^1H NMR (C_6D_6): δ 0.80 (d, 18 H, $^2J_{HP}$ = 7.5 Hz, 2 PMe_3), 1.58 (s, 6 H, CMe_2), 2.95 (t, 1 H, $^3J_{HP}$ = 13 Hz, Ni_2CH), 5.5-9.0 (m, 13 H, aromatics). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −15.6 s. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.0 (complex m, PMe_3), 34.8 (s, CMe_2), 57.2 (s, CMe_2), 111.4 (t, $^2J_{CP}$ = 9 Hz, Ni_2CH), 104.0, 106.0, 134.9, 135.0, 139.3, 141.0 (s, 1:2:1:2:2:1 ratio, CH pyrazolyl), 119.9, 123.1, 128.1, 148.9 (s, CH aromatics), 144.0 (t, $^2J_{CP}$ = 39 Hz, Ni_2C_{ar}), 167.1 (s, quaternary aromatic). Anal. Calcd for **7**: C, 48.9; H, 6.4; N, 13.8. Found: C, 49.6; H, 6.8; N, 13.1.

By a similar procedure but using $Tl[H_2B(3\text{-}t\text{-}Bu\text{-}pz)_2]$, compound **9** was obtained as dark red crystals in 67% yield. ^1H NMR (C_6D_6): δ 0.91 (d, 18 H, $^2J_{HP}$ = 7.1 Hz, 2 PMe_3), 1.21 (s, 18 H, 2 CMe_3), 1.55 (s, 6 H, CMe_2), 2.73 (t, 1 H, $^3J_{HP}$ = 13.8 Hz, Ni_2CH), 5.8–7.8 (m, 8 H, CH aromatics). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −18.0 s. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.0 (filled-in d, J_{CP}(app) = 20 Hz, 2 PMe_3), 31.4 (s, 2 CMe_3), 32.1 (s, 2 CMe_3), 34.3 (s, CMe_2), 57.6 (s, CMe_2), 103.5, 136.8 (s, 2 and 2 CH pyrazolyl), 108.0 (t, $^2J_{CP}$ = 10 Hz, $^1J_{CH}$ = 133 Hz, Ni_2CH), 119.7, 123.8, 128.1, 152.2 (s, CH aromatics), 141.2 (t, $^2J_{CP}$ = 40 Hz, Ni_2–C_{ar}), 160.7 (s, 2 CBu^t pyrazolyl), 166.5 (s, quaternary aromatic). Anal. Calcd for complex **8**: C, 54.6; H, 8.1; N, 8.5. Found: C, 55.3; H, 8.3; N, 8.5.

X-ray Structure Determination of Compound 2. A summary of the fundamental crystal data is given in Table IV. The crystals of **2** were dark red and prismatic and were twinned on (100) with *b* and *c* in common. One of these crystals (0.4 × 0.2 × 0.2 mm) was coated with epoxy resin and mounted on a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anaomalous dispersion correction for Ni, Cl, and P were taken from ref 46. The structure was solved by Patterson and Fourier methods. An empirical ab-

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(46) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 72.

Table VI. Final Fractional Coordinates for 3

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Ni1	0.569 42(11)	0.247 29(12)	0.026 27(6)	401(7)
Ni2	0.655 78(12)	0.208 69(11)	–0.026 73(7)	384(7)
Ni1B	0.195 44(13)	–0.003 53(12)	0.770 16(7)	448(7)
Ni2B	0.107 05(12)	0.024 66(11)	0.715 18(7)	435(8)
P1	0.613 82(32)	0.309 90(29)	0.078 15(15)	587(20)
P2	0.770 84(23)	0.243 71(25)	–0.042 21(14)	410(15)
P3	0.672 87(28)	0.088 00(24)	–0.028 23(19)	620(19)
P1B	0.166 42(39)	–0.081 17(35)	0.817 30(17)	807(25)
P2B	0.000 64(31)	–0.026 60(30)	0.695 04(16)	618(20)
P3B	0.069 29(32)	0.140 41(28)	0.712 25(17)	638(20)
Cl1	0.507 75(29)	0.169 86(31)	0.069 25(15)	726(21)
Cl1B	0.235 99(34)	0.080 67(30)	0.815 68(14)	770(22)
C1	0.624 38(87)	0.305 97(78)	–0.014 31(41)	327(54)
C2	0.563 67(95)	0.329 77(87)	–0.046 40(48)	426(59)
C3	0.514 84(93)	0.395 41(92)	–0.030 17(59)	576(69)
C4	0.605 19(105)	0.357 80(99)	–0.085 89(54)	645(74)
C5	0.514 75(91)	0.262 85(80)	–0.055 00(47)	360(56)
C6	0.529 10(82)	0.207 39(84)	–0.026 24(49)	340(50)
C7	0.478 57(97)	0.146 18(95)	–0.030 10(48)	467(61)
C8	0.426 10(115)	0.141 13(104)	–0.061 14(65)	601(76)
C9	0.416 04(116)	0.195 23(128)	–0.088 31(60)	697(87)
C10	0.459 54(112)	0.258 11(120)	–0.084 95(55)	634(79)
C11	0.544 66(172)	0.343 83(166)	0.113 62(90)	1387(153)
C12	0.680 60(145)	0.382 48(135)	0.072 42(75)	1069(120)
C13	0.671 81(163)	0.257 37(158)	0.113 61(83)	1298(139)
C21	0.797 74(109)	0.340 11(101)	–0.041 41(56)	637(77)
C22	0.845 29(120)	0.208 32(113)	–0.010 19(61)	758(86)
C23	0.806 06(115)	0.217 88(104)	–0.092 39(58)	700(83)
C31	0.621 43(154)	0.040 81(138)	–0.069 54(76)	1124(127)
C32	0.765 29(161)	0.041 80(148)	–0.037 26(81)	1220(136)
C33	0.634 85(164)	0.041 07(150)	0.017 46(80)	1264(142)
C1B	0.155 44(98)	–0.063 74(86)	0.726 79(50)	477(61)
C2B	0.221 88(124)	–0.077 50(109)	0.696 77(58)	688(83)
C3B	0.275 53(134)	–0.136 76(118)	0.712 24(78)	1005(108)
C4B	0.188 09(121)	–0.102 60(128)	0.655 93(64)	926(99)
C5B	0.259 77(104)	–0.003 66(107)	0.692 71(46)	501(65)
C6B	0.231 98(97)	0.047 48(88)	0.719 36(49)	429(61)
C7B	0.269 75(112)	0.116 40(107)	0.718 40(58)	632(78)
C8B	0.330 72(135)	0.127 96(132)	0.691 54(70)	803(98)
C9B	0.356 57(119)	0.074 09(173)	0.666 49(74)	867(111)
C10B	0.322 31(119)	0.008 02(162)	0.665 80(58)	857(105)
C11B	0.183 25(148)	–0.177 21(142)	0.810 56(77)	1150(112)
C12B	0.212 20(151)	–0.073 39(141)	0.867 19(78)	1138(133)
C13B	0.065 48(226)	–0.082 41(212)	0.825 02(116)	1940(225)
C21B	–0.079 68(123)	–0.009 58(117)	0.730 78(66)	882(100)
C22B	–0.037 93(124)	0.001 63(119)	0.646 50(65)	829(93)
C23B	–0.007 96(125)	–0.124 83(117)	0.689 70(65)	834(98)
C31B	0.109 89(128)	0.192 74(114)	0.671 41(64)	832(96)
C32B	0.094 19(133)	0.194 10(118)	0.757 63(69)	928(105)
C33B	–0.033 34(130)	0.168 42(122)	0.706 71(69)	921(104)

[a] See footnote *a* in Table V.

sorption correction[47] was applied at the end of the isotropic refinement. The refinement involved anisotropic thermal parameters for the non-hydrogen atoms, with the exception of the PMe$_3$ carbon atoms, which showed a nonresolved disorder and were refined isotropically. The hydrogen atoms were included with fixed contributions at their calculated positions; final R = 0.088, and $R(w)_F$ = 0.10. The maximum residual electronic density was 2 e Å^{-3} around the methyl groups. Most of the calculations were carried out with the X-Ray 80 system.[48]

Table VII. Final Fractional Coordinates for 5

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Ni1	0.741 08(6)	0.085 16(3)	0.663 93(3)	342(2)
Ni2	0.822 23(6)	0.129 34(3)	0.802 89(3)	319(2)
P1	0.748 35(13)	0.185 02)7)	0.910 01(7)	404(4)
P2	1.060 61(12)	0.159 97(7)	0.800 63(8)	435(4)
C1	0.864 11(46)	–0.001 20(24)	0.696 58(26)	373(13)
C2	0.992 98(49)	–0.025 30(27)	0.653 16(29)	459(15)
C3	1.071 46(55)	–0.092 99(31)	0.682 20(31)	549(17)
C4	1.022 37(61)	–0.136 74(30)	0.752 31(32)	592(19)
C5	0.893 21(58)	–0.115 04(28)	0.793 52(30)	527(17)
C6	0.813 81(46)	–0.048 04(24)	0.765 98(27)	384(13)
C7	0.668 14(49)	–0.020 69(26)	0.802 70(30)	454(15)
C8	0.654 67(43)	0.067 91(24)	0.775 00(26)	362(13)
C9	0.542 21(59)	–0.069 75(31)	0.760 10(42)	732(22)
C10	0.659 70(74)	–0.031 82(32)	0.901 61(35)	759(23)
C11	0.573 90(63)	0.103 14(35)	0.566 22(37)	686(21)
C12	0.704 02(70)	0.076 03(33)	0.526 31(31)	650(21)
C13	0.815 96(61)	0.132 96(32)	0.541 53(30)	578(18)
C14	0.756 68(59)	0.195 21(28)	0.590 48(32)	544(18)
C15	0.607 86(60)	0.176 97(31)	0.608 63(34)	597(19)
C16	0.774 37(60)	0.292 72(29)	0.922 49(35)	609(19)
C17	0.551 77(62)	0.181 21(35)	0.944 12(38)	732(22)
C18	0.831 03(76)	0.154 99(37)	1.023 41(33)	790(24)
C19	1.144 10(55)	0.242 46(32)	0.861 45(38)	644(20)
C20	1.149 51(61)	0.174 20(40)	0.696 89(39)	790(24)
C21	1.159 98(58)	0.075 39(34)	0.846 30(39)	695(21)

[a] See footnote *a* in Table V.

X-ray Structure Determination of Compounds 3 and 5. A summary of the fundamental crystal data are given in Table IV. Appropriate single crystals were coated with epoxy resin and mounted on a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, Cl, and P were taken from ref 46. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[47] was applied at the end of the isotropic refinement. The refinement involved anisotropic thermal parameters for the non-hydrogen atoms. Final refinement with fixed isotropic factors and coordinates for H atoms gave R_F = 0.063 and $R(w)_F$ = 0.067 (**3**) and R_F = 0.030 and $R(w)_F$ = 0.032 (**5**). Most of the calculations were carried out with the X-ray 80 system.[48]

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Supplementary Material Available: Tables of H atom coordinates and thermal parameters for compounds **2**, **3**, and **5** (7 pages). Ordering information is given on any current masthead page.

OM9302507

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(47) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(48) Stewart, J. M. *The X-Ray 80 System*; Computer Science Center, University of Maryland: College Park, MD, 1985.