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Binuclear Complexes of Nickel with the Bridging o-$CH_2C_6H_4$ Ligand: Synthesis and Reactions. X-ray Crystal Structure of *trans*-$(Me_3P)_2BrNi(C(\overline{O)C_6H_4\text{-}o\text{-}CH_2)Ni}Br(PMe_3)$, a Complex Containing a Bridging μ_2-η^1:η^1-Aroyl Ligand

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The reaction of Ni(cod)$(PMe_3)_2$ with equimolar amounts of $BrCH_2C_6H_4$-*o*-Br affords *trans*-Ni(η^1-$CH_2C_6H_4$-*o*-Br)Br$(PMe_3)_2$ (**1**), which oxidatively adds to a second equivalent of Ni(cod)$(PMe_3)_2$ to yield binuclear *cis,trans*-$(Me_3P)_2$BrNi(μ_2-η^1:η^1-CH_2-*o*-C_6H_4)NiBr$(PMe_3)_2$ (**2**). The latter complex readily loses one molecule of PMe_3 with the formation of the pseudoallyl *trans*-(Me_3P)BrNi(μ_2-η^3:η^1-CH_2-*o*-C_6H_4)-NiBr$(PMe_3)_2$ (**3**). Complex **2** selectively inserts CO into the Ni–benzyl bond (to give **4**), but under the same conditions, the pseudoallyl **3** furnishes a bridging aroyl, *trans*-$(Me_3P)_2BrNi(C(\overline{O)C_6H_4\text{-}o\text{-}CH_2)}$-NiBr$(PMe_3)$ (**6**), i.e., the product of the insertion of CO into the Ni–aryl bond. Complex **6** crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.907$ (1) Å, $b = 14.782$ (2) Å, $c = 24.660$ (3) Å, $\beta = 95.07$ (1)°, and $Z = 4$. The bridging aroyl ligand is characterized by C–O, Ni–C, and Ni′–O separations of 1.233 (18), 1.824 (16), and 1.982 (11) Å, respectively. Interaction of the pseudoallylic species **3** with PMe_3 produces the binuclear complex *trans,trans*-$(Me_3P)_2$BrNi(C_6H_4-*o*-CH_2CH_2-*o*-C_6H_4)NiBr$(PMe_3)_2$ (**7**), while the chelating ligands dmpm and dppm (dmpm = $Me_2PCH_2PMe_2$; dppm = $Ph_2PCH_2PPh_2$) yield respectively (dmpm)BrNi(μ_2-η^1:η^1-CH_2-*o*-C_6H_4)NiBr(dmpm) (**8**) and [(Me_3P)BrNi(μ_2-η^3:η^1-CH_2-*o*-C_6H_4)Ni)PMe_3)-(dppm)]Br (**9**). Obviously, compound **7** results from a C–C bond-forming reaction that involves the dimerization of the η^1-benzylic ligand through methylene coupling. The reaction of **3** with NaCp to give *trans*-$(C_5H_5)(PMe_3)$Ni(μ_2-η^1:η^1-CH_2-*o*-C_6H_4)NiBr$(PMe_3)_2$ (**10**) has also been studied.

Binuclear complexes in which the metallic centers are firmly held in close proximity by bridging hydrocarbon ligands are currently the subject of intense studies.[2] This is mainly due to the expectation that the cooperative effects between the two metal units may have a profound influence on the reactivity and other properties of these complexes. For many of these complexes, a requirement, sometimes achieved with considerable difficulty, is that the bridging ligand acts as an innocent spectator. In other cases, however, the linking chain is highly susceptible to further transformation, and this may give rise to interesting reactivity patterns.[3]

Alkyl and aryl complexes of Ni(II) can be conveniently prepared by the oxidative addition of the corresponding organic halides to Ni(0) precursors, in the presence of suitable stabilizing ligands.[4] We therefore reasoned that the use of the *o*-bromobenzyl bromide, $BrCH_2C_6H_4$-*o*-Br, could provide binuclear complexes of nickel in which the two nickel centers would be kept in close contact by means of the *o*-$CH_2C_6H_4$ biradical, through an arylic- and a benzylic-type interaction. Herein we wish to report the results of these studies which have allowed the isolation of binuclear complexes containing the bridging η^1:η^1- and η^3:η^1-CH_2-*o*-C_6H_4 ligands, as well as the investigation of their chemical properties. Benzyl-type ligands are known to exhibit a variety of coordination modes,[4c,5] including the $\pi + \sigma$ η^7-benzyl mode recently identified in a benzyl species adsorbed on a platinum surface.[6] Of these, the monohapto (i.e., *n*-alkyl) and the trihapto (pseudoallylic form) species, found for the complexes described in this contribution, are the most frequently encountered. Part of this work has been briefly communicated.[7]

Results and Discussion

The oxidative addition of *o*-bromobenzyl bromide, $BrCH_2C_6H_4$-*o*-Br, to in situ preformed Ni(cod)$(PMe_3)_2$ (from the room-temperature reaction of Ni$(cod)_2$ and PMe_3, 1:2 molar ratio; cod = 1,5-cyclooctadiene) affords the mononuclear complex **1** in good yields (eq 1). As

$$\mathrm{Ni(cod)(PMe_3)_2 + BrCH_2C_6H_4\text{-}\mathit{o}\text{-}Br \rightarrow \mathit{trans}\text{-}Ni(CH_2C_6H_4\text{-}\mathit{o}\text{-}Br)Br(PMe_3)_2 + cod} \quad (1)$$

expected, the reaction involves the weaker and more labile Br–benzyl bond. Compound **1** is an orange crystalline solid, fully characterized by microanalysis and spectroscopy (see Experimental Section). As it is commonly encountered in complexes of this type,[8] it is a highly fluxional molecule, to the point that, even at −60 °C, its $^{13}C\{^1H\}$ NMR spectrum shows a broad singlet for the methylene carbon of the benzylic ligand. The lack of resolvable coupling between this carbon and the ^{31}P nuclei is due to a very fast intermolecular phosphine-exchange process. The chemical shift of this resonance (12 ppm) is in

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

(2) (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. J. W. *Chem. Rev.* **1983**, *83*, 135. (b) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171. (c) Casey, C. P.; Andett, J. D. *Chem. Rev.* **1986**, *86*, 339.

(3) See, for example: (a) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Vollhardt, K. P. C.; Weidham, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676. (c) McGhee, W. D.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8428.

(4) (a) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501. (b) Klein, H. F.; Reitzel, L. *Chem. Ber.* **1988**, *121*, 1115. (c) Carmona, E.; Marín J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.

(5) Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 986.

(6) Avery, N. R. *J. Chem. Soc., Chem. Commun.* **1988**, 153.

(7) Cámpora, J.; Carmona, E.; Gutiérrez, E.; Palma, P.; Poveda, M. L.; Ruiz, C. *Organometallics* **1992**, *11*, 11.

(8) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285.

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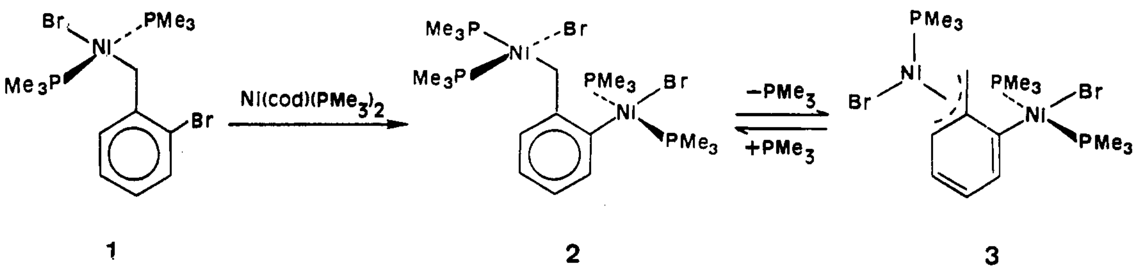
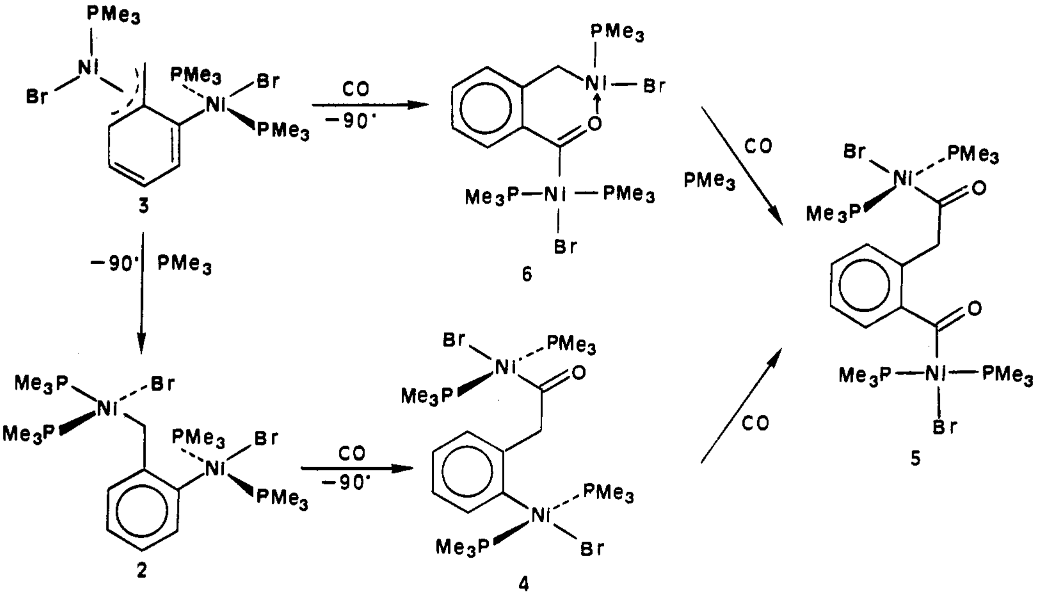
Scheme I



Scheme II



agreement with formulation of the complex as an η^1-benzylic derivative.[4c,8]

Compound 1 readily undergoes an oxidative addition reaction to a second equivalent of Ni(cod)$(PMe_3)_2$, with formation of binuclear 2 (Scheme I). The preparation of the latter species can be effected in a one-pot reaction, starting from Ni(cod)$(PMe_3)_2$ and $BrCH_2C_6H_4$-*o*-Br, without isolation of intermediate 1. Interestingly, 2 exists only in solution, removal of the solvent resulting in concomitant loss of PMe_3 and formation of a new binuclear species 3 (Scheme I), containing an aryl and a pseudoallyl functionality.

Compounds 2 and 3 have been fully characterized by NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P). For 2, the $^{31}P\{^1H\}$ NMR spectrum recorded at −90 °C shows two sets of resonances corresponding to an AB and an AX spin system. The former is characterized by a large $^{31}P-^{31}P$ coupling of 323 Hz, typical of mutually *trans*-phosphine ligands, while for the latter $^2J_{AX}$ is only of 9 Hz, indicating that these two PMe_3 groups occupy cis positions. Due to the highly fluxional character of 2, attempts to associate the above spin systems with the two Ni functionalities present in the molecules of 2 have proved unsuccessful. Hence, the proposed distribution of the PMe_3 ligands in 2 is somewhat speculative and it is based on the fact that related alkyl complexes of Ni containing bulky alkyl groups have cis geometry.[9] Regardless of the real nature of 2, it is evident that both the cis distribution of these PMe_3 ligands and the restricted rotation around the Ni–C_{ar} bond observed at −90 °C are due to steric congestion. At temperatures above −90 °C, the Ni–C_{ar} rotation becomes faster (as revealed by ^{31}P NMR studies), and at higher temperatures (around −5 °C), additional and more complicated PMe_3-exchange phenomena are operative.

Contrary to 2, the pseudoallyl 3 is a rigid molecule in solution which exhibits characteristic NMR features allowing its full characterization. Thus, the benzylic methylene carbon appears as a doublet at 31 ppm due to a small cisoid coupling to one ^{31}P nucleus ($^2J_{CP}$ = 8 Hz). The chemical shift of this resonance[4c,8] and the value of 152 Hz found for its one-bond C–H coupling constant[10] are clearly in accord with the proposed pseudoallylic structure. Furthermore, a relatively high-field aromatic resonance at 105 ppm can be attributed to the pseudoallylic aromatic CH carbon. Lastly, on these matters, the inequivalency of the *trans*-PMe_3 groups of the arylic moiety (see Experimental Section for relevant ^{13}C and ^{31}P NMR data) not only indicates restricted rotation around the Ni–aryl bond but it also reflects the absence of an antarafacial shift of the NiBr(PMe_3) fragment, a process invoked to explain the fluxionality of other η^3-benzylic complexes.[8,11] This mechanism implies usually the intermediacy of an η^1-benzyl by association of trace amounts of PMe_3, a process which seems unlikely in the system under consideration.

Carbon Monoxide Insertion Reactions. Work carried out in this and other laboratories has shown that alkyl and aryl complexes of Ni(II) containing PMe_3 ligands are specially prone to undergo carbonylation reactions with the formation of stable acyl species.[4c,8,12,13] The existence

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[9] $Ni(CH(SiMe_3)_2)Cl(PMe_3)_2$ has cis geometry as shown by X-ray crystallography. Carmona, E.; Gutiérrez, E.; Sernau, V. Unpublished work from these laboratories.

[10] (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574.

[11] Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845.

in complexes **2** and **3** of different kinds of Ni–C functionalities reveals some interesting selectivity during the insertion process. Scheme II summarizes the results obtained. Thus, complex **2** reacts with equimolar amounts of CO, at −80 °C, with selective insertion into the Ni–benzyl bond and formation of acyl **4**. The formulation proposed for **4** derives from the available spectroscopic data. In particular, the methylene group of the benzoyl moiety appears as a singlet at 64 ppm in the $^{13}C\{^1H\}$ NMR spectrum, while the Ni-bound aromatic carbon gives rise to a triplet at 159 ppm ($^2J_{CP}$ = 35 Hz). The observed selectivity for this reaction is in agreement with the higher kinetic propensity of the M–alkyl bonds, as compared to M–aryl, to undergo insertion of CO.[14] In the presence of an excess of CO, however, **4** reacts further to give relatively low yields (ca. 35%) of the unstable bis(acyl) **5** (Scheme II).

Interestingly, the analogous reaction of **3** with CO (1 equiv, −80 °C) yields the aroyl **6**, resulting from the selective insertion of CO into the Ni–aryl bond. The $^{31}P\{^1H\}$ NMR of this compound shows two singlets at −10.0 and −5.0 ppm (CD_2Cl_2) with relative intensities 2:1. These are respectively assigned to two mutually *trans*-PMe_3 groups (as revealed by the observation of a virtually coupled triplet in the ^1H NMR spectrum) and to a unique PMe_3 ligand. On the other hand, the $^{13}C\{^1H\}$ NMR spectrum shows a doublet for the benzylic methylene carbon (16.0 ppm, $^2J_{CP}$ = 30 Hz)[15] and a singlet at 141.4 ppm due to an aromatic quaternary carbon which splits into a doublet in the spectrum of a sample enriched in ^{13}CO (99% ^{13}CO, $^1J_{CC}$ = 33 Hz).[16] In addition, the acyl carbon gives a triplet at 271 ppm ($^2J_{CP}$ = 26 Hz).

The above data are in agreement with the structural formulation proposed for **6**. Moreover, the rather unusual values found for ν(C–O) and δ Ni–C(O)R of the Ni–acyl linkage (1510 cm^{-1} and 271 ppm, respectively; normal values of these parameters in other Ni–acyls are 1670–1600 cm^{-1} and ca. 250 ppm) and the existence of a single PMe_3 ligand bonded to the Ni–benzyl functionality suggest that this metal center attains a 16-electron configuration by virtue of an additional interaction with a lone pair of the acyl oxygen. Doubtless, the achievement of a stable, six-membered-ring configuration must contribute to the adoption of this coordination mode which, as discussed below, has been verified by X-ray crystallography.

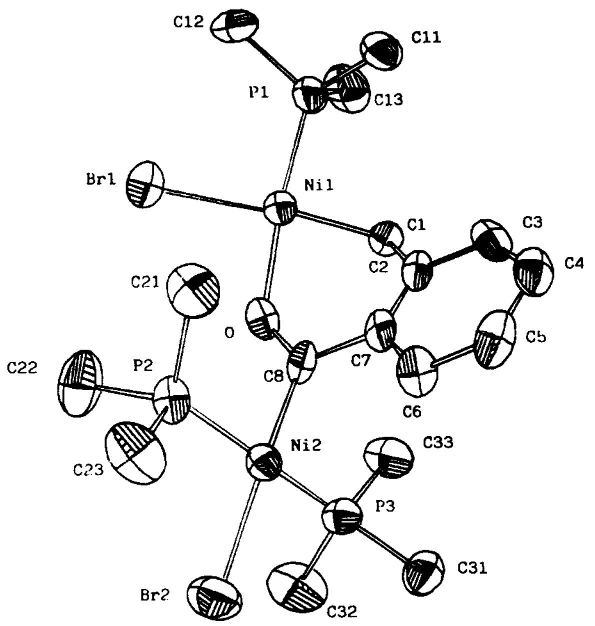

Figure 1. Molecular structure of the bridging aroyl derivative **6**.

Table I. Principal Bond Distances (Å) and Angles (deg) for 6

Ni1–Br1	2.356 (3)	P2–C23	1.789 (19)
Ni1–P1	2.120 (5)	P3–C31	1.800 (20)
Ni1–O	1.982 (11)	P3–C32	1.809 (20)
Ni1–C1	1.930 (15)	P3–C33	1.756 (21)
Ni2–Br2	2.354 (3)	O–C8	1.233 (18)
Ni2–P2	2.204 (5)	C1–C2	1.491 (22)
Ni2–P3	2.196 (5)	C2–C3	1.408 (22)
Ni2–C8	1.824 (16)	C2–C7	1.359 (22)
P1–C11	1.795 (19)	C3–C4	1.429 (25)
P1–C12	1.777 (22)	C4–C5	1.354 (26)
P1–C13	1.813 (23)	C5–C6	1.382 (24)
P2–C21	1.814 (20)	C6–C7	1.462 (22)
P2–C22	1.837 (20)	C7–C8	1.496 (21)
O–Ni1–C1	85.2 (6)	C1–C2–C7	122 (1)
P1–Ni1–C1	89.5 (5)	C1–C2–C3	119 (1)
P1–Ni1–O	174.0 (3)	C3–C2–C7	119 (1)
Br1–Ni1–C1	174.0 (5)	C2–C3–C4	121 (1)
Br1–Ni1–O	89.2 (3)	C3–C4–C5	118 (2)
Br1–Ni1–P1	96.3 (2)	C4–C5–C6	124 (2)
P3–Ni2–C8	90.7 (5)	C5–C6–C7	117 (1)
P2–Ni2–C8	88.0 (5)	C2–C7–C6	121 (1)
P2–Ni2–P3	175.1 (2)	C6–C7–C8	117 (1)
Br2–Ni2–C8	178.3 (5)	C2–C7–C8	122 (1)
Br2–Ni2–P3	90.1 (2)	O–C8–C7	118 (1)
Br2–Ni2–P2	91.4 (1)	Ni2–C8–C7	121 (1)
Ni1–O–C8	128 (1)	Ni2–C8–O	121 (1)
Ni1–C1–C2	108 (1)		

Although the similarity between **4** and **6** may suggest interconversion of both species under appropriate conditions, we have not succeeded in observing this transformation. Thus, complex **6** does not react with PMe_3, and on the other hand, heating **4** under vacuum results in its decarbonylation and partial decomposition. Compound **6** reacts, however, with CO to afford the bis(acyl) **5**. The above observations regarding the carbonylation of **2** and **3** indicate that the facility with which CO inserts into the Ni–C bonds of these complexes follows the order Ni–alkyl > Ni–aryl > Ni–pseudoallyl. Notwithstanding and having in mind the intramolecularly enhanced stabilization of **6**, some precautions should be taken upon attempting extrapolation of these results to other systems.

Figure 1 shows an ORTEP view of the molecules of **6**, including the atom numbering scheme. Table I collects important bond distances and angles. The two nickel

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(12) (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524. (b) Carmona, E.; González, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2108. (c) Carmona, E.; Paneque, M.; Poveda, M. L.; Rogers, R. D.; Atwood, J. L. *Polyhedron* **1984**, *3*, 317.

(13) For other NiCOR species, see, for example: (a) Fryzuk, M. D.; McNeil, P. A.; Rettig, S. J. *J. Organomet. Chem.* **1987**, *332*, 345. (b) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987**, *334*, 141. (c) Stavropoulos, P.; Carrié, M.; Muetterties, M. C.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5385.

(14) Alexander, J. J. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, Chapter 5.

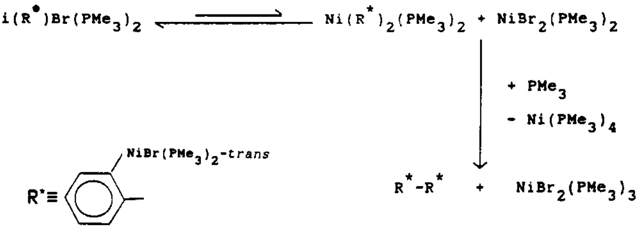
(15) The $^1J_{CH}$ value for this methylene carbon is 135 Hz. Although this coupling constant may seem rather high for a η^1-benzylic ligand (expected value ca. 125 Hz)[5,10] similar values have been found in several Ni-η^1-CH_2Ar complexes prepared in our laboratory. Also, some $CoCH_2Ar$ functionalities exhibit similar $^1J_{CH}$ couplings; see: Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834.

(16) $^1J_{CC}$ in CH_3COCH_3 is 40 Hz (Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR spectroscopy*; Wiley: New York, 1985). In transition-metal acyls, the corresponding $^1J_{CC(O)}$ coupling constant is somewhat variable: 36 Hz for Mo(η^2-$COCH_3$)Cl(CO)$(PMe_3)_3$ (Carmona, E.; Sánchez, L. Unpublished work from this laboratory); 5–19 Hz for some titanocene acyls (Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318. Mashima, K.; Haraguchi, H.; Ohyoshy, A.; Sakai, N.; Takaya, H. *Organometallics* **1991**, *10*, 2731 and references therein). In some instances, this constant can be even smaller, 1–3 Hz in $FeCOCH_2CMe_3$ complexes (Hermes, A. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 394).

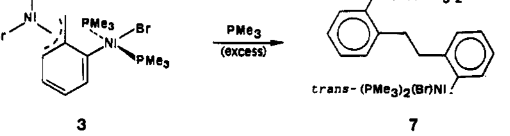
centers have distorted square-planar geometries, with the C atoms of the bridging hydrocarbon ligand in the two Ni moieties occupying trans positions with respect to the corresponding bromides. The puckered six-membered ring consists of the Ni1, C1, C2, C7, C8, and O atoms, and to accommodate the bridging aroyl ligand, both C8 and O atoms considerably deviate from the mean coordination planes of the nickel atoms to which they are bonded (0.81 and 0.89 Å, respectively). The dihedral angle between these planes is 38.72 (9)°. Bridging acyl ligands are relatively common for the early transition metals[17] but are much rarer in compounds of the later transition elements with the exception of the iron triad.[18] In many of the examples known for the earlier metals, the oxophilicity of the metal gives rise to a partial contribution of the oxycarbene structure, i.e., $MC(R){=}O \rightarrow M' \leftrightarrow M{=}C(R)OM'$, which consequently causes severe distortion of the bond distances within the MC(R)OM′ unit. For example, in the heterobinuclear species $Cp(OC)Mo(\mu\text{-}CO)(\mu\text{-}C(O)Me)\text{-}ZrCp_2$,[17a] the Mo–C separation (2.078 (3) Å) is considerably shorter than the 2.264 (14) Å value found for the η^1-acyl $CpMo(\eta^1\text{-}C(O)CH_3)PPh_3(CO)_2$. This oxycarbene character is further manifested by the values of ν(C–O) and δ Mo–*C*(O)R observed for the acyl functionality (1339 cm^{-1} and 317 ppm, respectively[17a]). No such deviations are found within the NiC(R)ONi unit of complex **6**. In fact, the C8–O separation of 1.233 (18) Å is equal within experimental error to that found in mononuclear Ni–aroyls (e.g., 1.22 Å[13a,b]). On the other hand, the Ni2–C8 distance of 1.824 (16) Å, while slightly shorter than the corresponding separation in Ni–aroyls (for instance, 1.878 (2) Å in $Ni(COPh)[N(SiMe_2CH_2PPh_2)_2]$;[13a] 1.859 (2) Å in $Ni(COPh)(Ph_2PC(Ph){=}C(OMe)O)(PEt_3)$[13b]), is clearly in the range normally found for acyl complexes of nickel (1.84 (2) Å (average) in *trans*-$Ni(C(O)CH_2SiMe_3)Cl(PMe_3)_2$;[12b] 1.84 Å in $Ni(C(O)CH_3)Cl(PMe_3)_2$[12a]). Therefore, the somewhat anomalous values of ν(C═O) and δ *C*(R)═O must be attributed to the existing dative bond. In addition, the absence of any important Ni═C bond character is also indicated by the fast rotation around this Ni—C bond as shown by NMR spectroscopy. Bond distances and angles within the coordination spheres of the two metal atoms have normal values. For example, the Ni–CH$_2$ (Ni1–C1 = 1.930 (15) Å) compares well with corresponding distances in other related complexes (e.g., 1.95 (1) Å (average) in $Ni_3(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu\text{-}OH)_2$[4c]). On the other hand, the Ni1–O bond length of 1.982 (11) Å resembles more that found in complexes of Ni with neutral O donors (ca. 2.0 Å[19]) than those associated to the stronger Ni–O bonds with monoanionic O ligands (for example, 1.914 (4) Å in $Ni(OC(OMe){=}C(Ph)PPh_2)(Ph)(PEt_3)$[13b]).

Other Reactions of Compounds 2 and 3. In some instances, the reaction leading to the binuclear complex **2** provided in addition small amounts of a yellow microcrystalline solid, identified as the binuclear species

Scheme III



trans,trans-$(Me_3P)_2BrNi(C_6H_4\text{-}o\text{-}CH_2CH_2\text{-}o\text{-}C_6H_4)NiBr(PMe_3)_2$ (**7**). It was soon realized that an excess of PMe$_3$, inadvertently introduced in the reaction mixture, was responsible for this transformation and, in fact, **7** is best prepared by treatment of **2** or **3** with an excess of PMe$_3$ (eq 2). Characterization of **7** from the spectroscopic data



(2)

3 **7**

given in the Experimental Section is straightforward and needs no additional comments. It is worth pointing out, however, that the observed transformation constitutes an interesting example of a C–C bond-forming reaction by reductive dimerization of a benzylic ligand. Reductive coupling of alkyl and/or aryl functionalities is a very common process in organometallic chemistry.[20] The above reaction is, however, unusual in the sense that the hydrocarbon ligand is bonded to a second metal center which acts as an innocent spectator; that is, it does not become involved in the reaction. This allows the isolation of the binuclear compound **7**. Note that this synthetic methodology may be potentially useful for the preparation of related Ni–aryls that cannot be obtained by conventional procedures. Byproducts of the above transformation are $NiBr_2(PMe_3)_3$ and $Ni(PMe_3)_4$. A possible route for the formation of these materials is shown in Scheme III. The proposed pathway finds precedent in a related reaction undergone by the benzylic complex $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Br(PMe_3)_2$, which affords 1,2-bis(2-methylphenyl)ethane, $C_{16}H_{18}$, together with $NiBr_2(PMe_3)_3$ and $Ni(PMe_3)_4$.[4c]

The reactions of the pseudoallylic complex **3** with the small-bite, chelating phosphines dmpm and dppm ($R_2PCH_2PR_2$, R = Me (dmpm); R = Ph (dppm)) proceed according to Scheme IV, i.e., with the formation of the new compounds **8** and **9**, respectively. The symmetric distribution proposed for the dmpm ligands in **8** is best inferred from the $^{31}P\{^1H\}$ NMR spectrum of this complex, which consists of an AA′BB′ spin system, with strongly coupled isochronous ^{31}P nuclei ($^2J_{AA'} = {}^2J_{BB'} \simeq 450$ Hz), clearly indicating their trans arrangement. Also in accord with this proposed structure is the observation of the eight methyl–phosphine groups paired into four sets of signals, both in the ^1H and $^{13}C\{^1H\}$ NMR.

As shown in Scheme IV, the reaction of **3** with dppm takes a different course and yields a catonic species **9**, in which the bromide and one of the PMe$_3$ ligands of the arylic moiety have been substituted by the chelating phosphine. Interestingly, the benzylic part of the molecule remains unaltered and this is probably due to the steric

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[18] See, for example: (a) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826. (b) Rosen, R. P.; Hocke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846. (c) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I. *J. Organomet. Chem.* **1986**, *307*, 61. (d) Hoke, J. B.; Dewan, J. C.; Seyferth, D. *Organometallics* **1987**, *6*, 1816.

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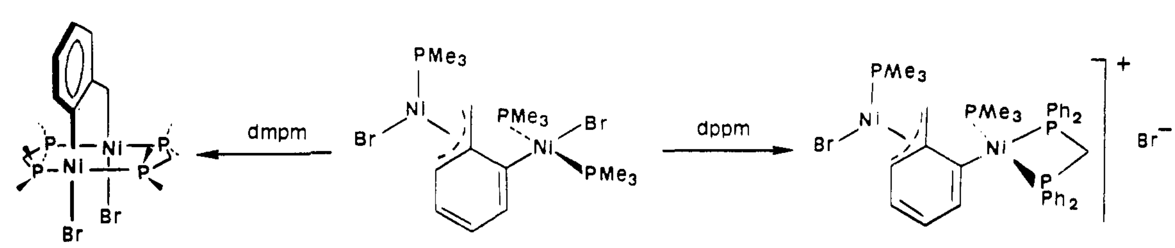
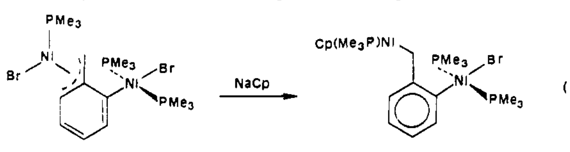
Scheme IV



8 3 9

bulkiness of the dppm ligand. Both the chemical shift of the methylene carbon and the value of $^1J_{CH}$ for this group (49 ppm and 154 Hz, respectively) are in accord with the proposed structure. Interestingly, this CH_2 experiences long-range coupling (four bonds) to two of the ^{31}P nuclei ($^4J_{CP}$ = 7 Hz).

Finally, NaCp attacks the pseudoallyl moiety of **3** with the formation of **10** (eq 3). This complex is a stable molecule, with no tendency to undergo loss of PMe_3 and formation of a Cp–pseudoallyl complex. With this respect, we note that although some CpNi(η^3-benzylic) compounds are known,[21] they are usually unstable and tend to add a neutral ligand to form the corresponding η^1-benzylic structures.[4c]



(3)

3 10

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Remagen, Germany, and the Microanalytical Service of the University of Sevilla. Perkin-Elmer Models 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_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenck techniques. Solvents were dried and degassed before use. $Ni(cod)_2$[22] and PMe_3[23] were prepared by published methods.

Synthesis of *trans*-Ni(η^1-$CH_2C_6H_4$-*o*-Br)Br(PMe_3)$_2$ (1). To a stirred suspension of $Ni(cod)_2$ (0.55 g, 2 mmol) in Et_2O (70 mL) was added 0.4 mL of PMe_3 (4 mmol). After the solution was stirred at room temperature for 2–3 h, the resulting pale yellow solution was cooled at −80 °C and a toluene solution of $BrCH_2C_6H_4$-*o*-Br (2.0 mL of a 1 M solution) was slowly introduced into the flask. The cooling bath was removed, and after warming at room temperature, the solution was filtered and the filtrate concentrated under reduced pressure and cooled at −30 °C. Complex **1** was isolated as an orange crystalline solid in 75% yield. ^1H NMR (CD_2Cl_2, 20 °C) δ 1.25 (br s, 18 H, 2 PMe_3), 1.87 (br s, 2 H, CH_2), 7.0–7.9 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −8.8 (br s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 10.3 (br s, PMe_3), 12.0 (br s, CH_2), 121.1, 121.8, 123.8, 127.8 (s, CH aromatics). Anal. Calcd for $C_{13}H_{24}P_2Br_2Ni$: C, 33.9; H, 5.2. Found: C, 33.2; H, 5.4.

Synthesis of Complex 3. $Ni(cod)_2$ (1.1 g, 4 mmol) in 80 mL of Et_2O was treated with PMe_3 (0.6 mL, 6 mmol) as above. Without stirring, 2 mL of a 1 M toluene solution of $BrCH_2C_6H_4$-*o*-Br was then added and the resulting mixture left undisturbed for 4–5 h. The precipitated red-orange crystals were collected and dried in vacuo (60–70% yield). From the mother liquor, an additional crop (10–20% yield) could be obtained. ^1H NMR (CD_2Cl_2, 20 °C) δ 1.02 (br d, 9 H, $^2J_{HP}$ = 5.9 Hz, PMe_3), 1.47 (br d, 18 H, J_{HP}(app) = 9.1 Hz, 2 PMe_3), 3.04, 3.66 (br m, br m, 1 H, 1 H, CH_2), 6.4–7.3 (br m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ −12.8 and −7.4 (AB spin system, $^2J_{AB}$ = 398 Hz, 2 *trans*-PMe_3), −5.0 (s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ 13.1 (dd, $^1J_{CP}$ = 24, $^3J_{CP}$ = 5 Hz, PMe_3), 14.8 (dd, $^1J_{CP}$ = 24, $^3J_{CP}$ = 5 Hz, PMe_3), 15.7 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 30.5 (d, $^2J_{CP}$ = 8, $^1J_{CH}$ = 152 Hz, CH_2), 105.1 (d, $^2J_{CP}$ = 11 Hz, CH aromatic bound to Ni), 119.9 (d, $^2J_{CP}$ = 6 Hz, quaternary aromatic bound to Ni), 126.4, 127.3, 139.0 (s, CH aromatics), 166.5 (t, $^2J_{CP}$ = 34 Hz, C_qNi). Anal. Calcd for $C_{16}H_{33}P_3Br_2Ni_2$: C, 32.3; H, 5.5. Found: C, 31.8; H, 5.5.

Complex **3** cleanly reacted with 1 equiv of PMe_3 to give **2**, a species stable only in solution. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): an AX spin system with δ_A −18.3, δ_X −3.5, $^2J_{AX}$ = 9 Hz and an AB spin system with δ_A −11.4, δ_B −3.6, $^2J_{AB}$ = 323 Hz.

Synthesis of the Monoacyl 4. Complex **2** was prepared in situ from the pseudoallylic species **3** (0.77 g, 1.3 mmol) and PMe_3 (0.13 mL, 1.3 mmol) in 80 mL of THF. The resulting solution was cooled to −90 °C and 31 mL of carbon monoxide introduced via syringe. The cooling bath was removed, and after 30 min of stirring at 20 °C, the solution was taken to dryness. The resulting residue was extracted with Et_2O and filtered. After concentration and cooling at −30 °C, complex **4** was obtained in 65% yield as an orange crystalline material. IR (Nujol mull) ν(C=O) 1650 (s) cm^{-1}; ^1H NMR (CD_2Cl_2, 20 °C) δ 1.08 (br s, 18 H, 2 PMe_3), 1.34 (br s, 18 H, 2 PMe_3), 5.04 (s, 2 H, CH_2), 6.7–7.4 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) δ −10.7 (s, 2 PMe_3), −6.2 (s, 2 PMe_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, −90 °C) δ 12.2 (pseudotriplet, J_{CP}(app) = 14 Hz, 2 PMe_3), 13.2 (pseudotriplet, J_{CP}(app) = 14 Hz, 2 PMe_3), 64.1 (s, COCH_2), 120.4, 123.4, 126.5, 133.9 (s, s, s and t, J_{CP} = 5 Hz, CH aromatics), 138.8 (s, quaternary aromatic), 159.0 (t, $^2J_{CP}$ = 35 Hz, C_qNi), 252.0 (s, *C*OCH_2). Anal. Calcd for $C_{20}H_{42}OP_4Br_2Ni_2$: C, 34.3; H, 6.0. Found: C, 34.3; H, 6.2.

Synthesis of the Bis(acyl) 5. This complex was obtained following an identical procedure to that described above for the synthesis of **4**. In this case, however CO was bubbled for a few minutes. Crystallization from Et_2O furnished **5** as orange crystals in 35% yield. IR (Nujol mull) ν(C=O) complex pattern from 1585 to 1690 cm^{-1}; ^1H NMR (CD_3COCD_3, −80 °C) δ 1.11 (pseudotriplet, 18 H, J_{HP}(app) = 4.0 Hz, 2 PMe_3), 1.28 (pseudotriplet, 18 H J_{HP}(app) = 5.1 Hz, 2 PMe_3), 4.70 (br s, 2 H, CH_2), 7.1–7.7 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_3COCD_3, −80 °C) δ −5.8 (s, 2 P), −5.2 (s, 2 P); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 20 °C) δ 14.0 (br s, PMe_3), 52.3 (s, CH_2), 127.0, 130.8, 132.3, 137.9 (s, CH aromatics). Quaternary carbons were not located. Anal. Calcd for $C_{21}H_{42}O_2P_4Br_2Ni_2$: C, 34.6; H, 5.8. Found: C, 35.2; H, 5.9.

Synthesis of the Bridging Aroyl 6. A solution of **3** (0.89 g, 1.5 mmol) in THF (70 mL) was cooled to −90 °C and 33.6 mL of carbon monoxide introduced into the flask via syringe. After the solution was warmed to room temperature, the stirring was continued for 30 min. The solvent was eliminated under reduced pressure and the residue stirred with 20 mL of Et_2O, filtered, and washed with 20 mL of petroleum ether. The resulting crude dark red microcrystalline product was recrystallized from Et_2O–acetone. Yield: 70%. IR (Nujol mull) ν(C=O) 1510 (s) cm^{-1}; ^1H NMR (CD_2Cl_2, 20 °C) δ 1.26 (d, 9 H, $^2J_{HP}$ = 9.9 Hz, PMe_3), 1.31 (pseudotriplet, 18 H, J_{HP}(app) = 4.1 Hz, 2 PMe_3), 1.69 (d, 2 H, $^3J_{HP}$ = 9.4 Hz, CH_2), 7.0–8.9 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −10.0 (s, 2 P), −5.0 (s, 1 P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2,

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20 °C) δ 13.3 (pseudotriplet, J_{CP}(app) = 15 Hz, 2 PMe_3), 14.9 (d, $^1J_{CP}$ = 32 Hz, PMe_3), 16.0 (d, $^2J_{CP}$ = 30, $^1J_{CH}$ = 135 Hz, CH_2), 123.6, 126.4, 132.4, 135.1 (s, CH aromatics), 140.5, 141.4 (s, quaternary aromatics), 270.9 (t, $^2J_{CP}$ = 26 Hz, NiCOAr). ^{13}CO-enriched sample: IR (Nujol mull) $\nu(^{13}C{=}O)$ 1485 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −10.0 (d, $^2J_{CP}$ = 27 Hz, 2 P), −5.0 (s, P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) 141.4 (d, $^1J_{CC}$ = 33 Hz, C_qCONi). Anal. Calcd for $C_{17}H_{33}OP_3Br_2Ni_2$: C, 32.7; H, 5.3. Found: C, 32.6; H, 5.3.

Synthesis of the Binuclear Aryl Derivative 7. Complex 3 (0.30 g, 0.5 mmol) was dissolved in the minimum volume of THF, and 1 mL of PMe_3 (an excess) was added, with stirring, at room temperature. After a few minutes, the reaction mixture developed a dark blue color, and the stirring was continued for a further 1 h. The volatiles were removed in vacuo, and the residue was extracted with CH_3OH until the extracts were no longer blue. The insoluble yellow microcrystalline solid that resulted was washed with petroleum ether and dried in vacuo. Yield: 70%. The microanalytical sample was recrystallized from hot CH_2Cl_2. ^{1}H NMR (CD_3COCD_3, 20 °C) δ 1.12 (pseudotriplet, 18 H, J_{HP}(app) = 3.7 Hz, 2 PMe_3), 3.72 (s, 2 H, CH_2), 6.8–7.4 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −13.1 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 13.6 (pseudotriplet, J_{CP}(app) = 15 Hz, PMe_3), 40.5 (s, CH_2), 121.9, 124.4, 126.2, 134.1 (s, CH aromatics). Quaternary carbons were not located. Anal. Calcd for $C_{28}H_{48}P_4Br_2Ni_2$: C, 40.9; H, 6.3. Found: C, 40.6; H, 6.0.

Reaction of Complex 3 with dmpm. Synthesis of 8. To a cold (−80 °C), stirred solution of 3 (0.33 g, 0.55 mmol) in THF (50 mL) was added dropwise a solution of dmpm in THF (1.1 mmol). The resulting mixture was stirred for 1 h at room temperature, the solvent stripped off, and the residue extracted with 30 mL of toluene. An unidentified orange solid was separated by filtration and the filtrate reduced in volume. After 10 mL of Et_2O was added, the solution was cooled to −30 °C to obtain complex 8 as a red crystalline solid in 20% yield. ^{1}H NMR (CD_3COCD_3, 20 °C) δ 0.95 (pt, 6 H, J_{HP}(app) = 3.0 Hz, 2 PMe), 1.36 (pt, 6 H, J_{HP}(app) = 2.5 Hz, 2 PMe), 1.69 (pt, 6 H, J_{HP}(app) = 3.6 Hz, 2 PMe), 1.71 (pt, 6 H, J_{HP}(app) = 3.6 Hz, 2 PMe), in this PMe region some complex multiplets are probably due to the $NiCH_2$ and PCH_2 protons, 6.5–7.5 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 20 °C) AA′BB′ spin system. The following parameters were obtained from a successful computer simulation: $\delta_A = -3.8$, $\delta_B = -4.5$, $J_{AA'} = J_{BB'} \simeq 450$, $J_{AB} = J_{A'B'} \simeq 58$, $J_{AB'} = J_{A'B} \simeq 2$ Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 13.0–16.4 (complex multiplets, PMe and $NiCH_2$), 30.0 (pseudoquintet, J_{CP}(app) = 11 Hz, PCH_2), 121.6, 123.0, 127.7, 135.3 (s, CH aromatics), 152.9 (s, quaternary aromatic carbon), 156.0 (t, $^2J_{CP}$ = 29 Hz, C_qNi). Anal. Calcd for $C_{17}H_{34}P_4Br_2Ni_2$: C, 32.1; H, 4.7. Found: C, 31.2; H, 5.0. Owing to the limited amounts of 8 available and to the difficulty of its purification by recrystallization, the corresponding analytical figures are somewhat deviated from those expected. It must be noted, however, that the diamagnetic impurities in the crude sample could only be present in trace amounts (NMR evidence).

Reaction of Complex 3 with dppm. Synthesis of 9. A solution of complex 3 (1.49 g, 2.5 mmol) in 70 mL of CH_2Cl_2 was cooled at −60 °C and treated with 1.15 g of dppm dissolved in 10 mL of the same solvent. After 1 h of stirring at room temperature, the mixture, which contained a precipitate of complex 9, was taken to dryness and the residue washed three times with 25 mL of toluene. The resulting red microcrystalline product (80% yield) was recrystallized from CH_2Cl_2–THF. ^{1}H NMR (CD_3COCD_3, 20 °C) δ 0.88 (dd, 9 H, $^2J_{HP}$ = 10.5, $^4J_{HP}$ = 1.8 Hz, PMe_3), 1.17 (t, 2 H, $^2J_{HP}$ = 6.8 Hz, PCH_2), 1.37 (d, 9 H, $^2J_{HP}$ = 9.8 Hz, PMe_3), 3.35 and 3.72 (m, 1 H and 1 H, $NiCH_2$), 6.0–8.4 (m, 24 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −8.5 (dd, $^2J_{PP}$ = 380 and 32 Hz, PMe_3), −3.7 (s, PMe_3), 27–34 (m, 2 PPh_2); $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C) δ 14.2 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 16.4 (d, $^1J_{CP}$ = 31 Hz, PMe_3), 28.1 (t, $^1J_{CP}$ = 22 Hz, PCH_2), 48.7 (dt, $^2J_{CP}$ = 20, $^4J_{CP}$ = 7, $^1J_{CH}$ = 154 Hz, $NiCH_2$), 128–150 (aromatics); the C_qNi carbons could not be assigned. Anal. Calcd for $C_{38}H_{46}P_4Br_2Ni_2$: C, 51.6; H, 5.5. Found: C, 51.5; H, 5.5.

Reaction of 3 with NaCp. Synthesis of the Cyclopentadienyl Derivative 10. To a solution of complex 3 (0.7 mmol) in THF (50 mL) cooled to −70 °C was added NaCp (2.2 mL of a 0.32 M solution in THF, 0.7 mmol). After the solution was warmed to room temperature, the stirring was continued for 2 h. The suspension was taken to dryness and the residue extracted with Et_2O (80 mL) and filtered. After concentration and cooling at −30 °C, complex 10 was obtained in 61% yield as green crystals. ^{1}H NMR (CD_2Cl_2, 20 °C) δ 1.12 (pt, 18 H, J_{HP}(app) = 3.8 Hz, 2 PMe_3), 1.39 (d, 9 H, $^2J_{HP}$ = 9.2 Hz, PMe_3), 2.48 (d, 2 H, $^3J_{HP}$ = 10.2 Hz, CH_2), 4.92 (s, 5 H, C_5H_5), 6.5–6.9 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −10.1 (s, 2 P), 0.4 (s, P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 3.5 (d, $^2J_{CP}$ = 21 Hz, CH_2), 13.9 (pseudotriplet, J_{CP}(app) = 14 Hz, 2 PMe_3), 17.7 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 90.8 (s, C_5H_5), 120.6, 121.0, 128.0, 134.1 (CH aromatics), 152.4 (t, $^2J_{CP}$ = 31 Hz, C_qNi), 158.1 (quaternary aromatic). Anal. Calcd for $C_{21}H_{38}P_3BrNi_2$: C, 43.4; H, 6.5. Found: C, 43.6; H, 6.7.

Table II. Crystal and Refinement Data for 6

formula	$C_{17}H_{33}OP_3Br_2Ni_2$
M	623.6
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	6.907 (1)
b, Å	14.782 (2)
c, Å	24.660 (3)
β	95.07 (1)
V, Å^3	2507.9 (6)
Z	4
F(000)	1256
ρ(calcd), g cm^{-3}	1.65
temp, °C	22
μ, cm^{-1}	48.6
cryst dimens, mm	0.3 × 0.2 × 0.2
diffractometer	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
scan technique	$\vartheta/2\theta$ ($1 < \vartheta < 25$)
data collected	(−8, 0, 0) to (8, 17, 29)
no. of rflns collected	4878
no. of unique data	4387
no. of obsd data ($I > 2\sigma(I)$)	2514
R(int), %	0.8
no. of std. rflns	3/176
R_F, %	6.5
$R(w)_F$, %	7.0
av shift/error	0.04

Table III. Final Fractional Coordinates for 6 (U_{eq} × 10^4)

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ni1	0.82991 (28)	0.24224 (13)	0.20415 (8)	341 (6)
Ni2	1.11355 (28)	0.21579 (13)	0.04295 (8)	347 (6)
Br1	0.86095 (29)	0.08654 (13)	0.22349 (8)	573 (7)
Br2	1.23998 (33)	0.15908 (16)	−0.03584 (8)	685 (8)
P1	0.75812 (73)	0.28170 (32)	0.28258 (19)	476 (16)
P2	1.29441 (61)	0.12177 (29)	0.09505 (19)	409 (14)
P3	0.91178 (63)	0.30222 (31)	−0.00764 (18)	416 (14)
O	0.90686 (148)	0.21828 (69)	0.12998 (44)	410 (36)
C1	0.80263 (224)	0.36632 (105)	0.18044 (63)	407 (54)
C2	0.99426 (218)	0.39708 (100)	0.16378 (63)	386 (51)
C3	1.07580 (264)	0.47766 (115)	0.18597 (67)	494 (62)
C4	1.25705 (273)	0.51117 (121)	0.17064 (75)	520 (65)
C5	1.34349 (228)	0.46500 (119)	0.13194 (81)	514 (65)
C6	1.27404 (202)	0.38475 (110)	0.10898 (71)	424 (57)
C7	1.09396 (230)	0.34965 (100)	0.12814 (64)	400 (53)
C8	1.02271 (211)	0.26118 (99)	0.10467 (65)	371 (52)
C11	0.91937 (290)	0.36569 (131)	0.31372 (72)	608 (72)
C12	0.76019 (454)	0.19645 (156)	0.33352 (81)	1002 (117)
C13	0.51745 (323)	0.33002 (152)	0.28426 (92)	807 (93)
C21	1.35238 (271)	0.14898 (142)	0.16638 (81)	652 (76)
C22	1.14836 (285)	0.01863 (135)	0.09933 (99)	750 (88)
C23	1.52753 (252)	0.08938 (154)	0.07518 (90)	720 (83)
C31	1.04362 (295)	0.39173 (127)	−0.03746 (77)	621 (73)
C32	0.77970 (285)	0.24884 (169)	−0.06555 (78)	779 (86)
C33	0.72932 (294)	0.36328 (145)	0.02165 (74)	677 (78)

X-ray Structure Determination. A summary of the fundamental crystal data is given in Table II. A single crystal of 6 was resine epoxy coated and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting 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, Br, and P were taken from ref 24. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[25] was applied at the end of the isotropic refinement. Final refinement with fixed isotropic factors and coordinates for H atoms gave $R_F = 0.065$ and $R(w)_F = 0.070$. Most of the calculations were carried out with the X-Ray 80 system.[26]

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Registry No. 1, 141612-15-9; 2, 141612-16-0; 3, 137515-87-8; 4, 141612-17-1; 5, 141612-18-2; 6, 141612-19-3; 7, 141612-20-6; 8, 137515-89-0; 9, 141612-21-7; 10, 141612-22-8; Ni(cod)$_2$, 1295-35-8; BrCH$_2$C$_6$H$_4$-*o*-Br, 3433-80-5.

Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **6** (2 pages). Ordering information is given on any current masthead page.

OM910705X

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Mechanism for the Exchange Processes Observed in the Compounds [M(η-C$_5$H$_5$)$_2$(η-RCH=CH$_2$)H] (M = Nb, Ta)

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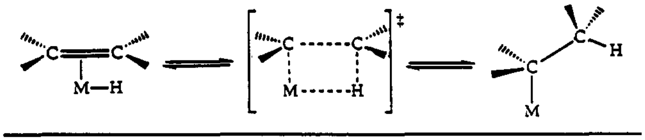
The fluxional processes in the compounds *exo*-[M(η-C$_5$H$_5$)$_2$(η-CH$_3$CH=CH$_2$)H] (M = Nb, Ta) have been investigated by magnetization and spin-saturation transfer and two-dimensional exchange NMR techniques. Rate constants for three separate processes have been determined. A mechanism involving agostic η^2-alkyl ligands is proposed.

Bercaw and co-workers recently reported a NMR study of the dynamic processes in the olefin–hydride complexes [M(η-C$_5$R″$_5$)$_2$(η-RCH=CH$_2$)H] (M = Nb, Ta) and proposed a multistep mechanism to account for the data.[1] We have made studies of the similar dynamic behavior of other olefin–hydride–metal systems, and these have provided evidence for the occurrence of intermediates with agostic bonds and in-place rotation of agostic metal–alkyl groups.[2] We were interested to see if agostic intermediates can also account for the dynamic processes oberved for the niobium and tantalum systems. We deemed such a study to be worthwhile since the insertion of olefins into the metal–hydride bonds in olefin–hydride complexes and its microscopic reverse, β-elimination, are reactions of fundamental importance in organometallic chemistry and are key steps in such industrial catalytic processes as hydroformylation, olefin hydrogenation, and isomerization.[3,4]

A preliminary account of this work has been reported.[5]

Background

The mechanism generally proposed for the reversible insertion of an olefin into a metal–hydride bond[3,4] proceeds via a planar, delocalized cyclic transition state in which the migrating hydrogen is bonded to both the metal center and to one of the olefinic carbons, thus resulting in overall cis addition of the metal–hydride to the double bond:[6]



Strong supporting evidence for this delocalized transition state (or intermediate) comes from the discovery of transition-metal–alkyl complexes with β-agostic interactions in which this delocalized structure is adopted in the ground state.[7] Indeed, many complexes which were previously assigned ethylene–hydride structures have since been shown to be agostic ethyl complexes with 2e–3c M–H–C$_\beta$ interactions.

Since olefin insertions are often reversible and not rate-limiting, direct measurements of their kinetics in reaction sequences are difficult. Notably, however, Halpern and co-workers have been successful in measuring the rate of olefin insertion into rhodium–hydride bonds in the reaction of various olefins with a number of rhodium complexes.[8,9] Reversible intramolecular olefin insertion resulting in mutual exchanges has been observed by variable-temperature NMR spectra and/or by deuterium labeling, and in some cases the rate constants and activation

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