Organometallics **2008,** *27,* 1834–1840

P−C Bond Scission at the TRIPHOS Ligand and C−CN Bond Cleavage in 2-Methyl-3-butenenitrile with [Ni(COD)$_2$]

Alberto Acosta-Ramírez,[†] Marcos Flores-Álamo,[†] William D. Jones,[‡] and Juventino J. García[†,*]

Facultad de Química, Universidad Nacional Autónoma de México, México City, México D.F. 04510, and Department of Chemistry, University of Rochester, Rochester, New York, 14627

Received November 13, 2007

The use of catalytic amounts of [Ni(COD)$_2$] and TRIPHOS (bis(2-diphenylphosphinoethyl)phenylphosphine) allows the isomerization of 2-methyl-3-butenenitrile (2M3BN) at 100 °C, to yield *Z*- and *E*-2-methyl-2-butenenitrile (2M2BN) (57% and 31%, respectively), small amounts of 3-pentenenitrile (3PN) (5%), along with a mixture of nickel complexes, consisting of *cis*- and *trans*-[Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$(CN)$_2$] (**1**, **2**), *cis*- and *trans*-[Ni(TRIPHOS)(CN)$_2$] (**3**, **4**), [Ni(TRIPHOS)] (**5**), and [Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$] (**6**), where compounds **1**–**4** and **6** are the C−CN and P−C bond cleavage products, respectively. The persistent presence of benzene in the reaction mixture was confirmed by GC-MS. The use of stochiometric amounts of the reagents led to the isomerization of 2M3BN to *Z*- and *E*-2M2BN (47% and 44%, respectively) and 3PN (9%); the formation of complexes **2**, **5**, and **6** has been confirmed to take place, in addition to benzene and 1,3-butadiene. Complexes **1** and **3** were characterized by single-crystal X-ray determinations.

Introduction

The development of organometallic chemistry and homogeneous catalysis with transition metals has long been assisted by the use of omnipresent phosphine ligands, providing their great versatility and capability to stabilize a variety of metal centers in different oxidation states and geometries. The applicability of phosphine ligands has been particularly highlighted as a result of the possibilities offered by these ligands to assist in a wide variety of metal-mediated and metal-catalyzed bond cleavage and formation reactions involving different substrates,[1] and in many cases, some rather complicated transformations have been achieved. Among the diversity of possible combinations that phosphine ligands offer for such transformations, PPh$_3$ is by far the most frequently used. However, under certain circumstances it has been reported that both triaryl and trialkyl phosphine ligands may react with metal centers upon coordination, the stoichiometric cleavage of both C−H and P−C bonds of the ligands having been reported to take place effectively: C−H ortho-metallated complexes been reported to form in the case of some aryl phosphines, while phosphido-bridged derivatives have been found in the case of other trialkyl phosphine ligands. The latter processes have been associated with the deactivation of the catalytic species in homogeneous processes and a wealth of examples have been provided in the literature.[2] In the case of P−C bond cleavage reactions, the vast majority of the documented data involves aryl and alkyl monophosphine ligands, and their activation has been reported to take place in the presence of clusters,[3] as well as in the presence of homo-[4] and heterobimetallic complexes.[5] Also, P−C bond cleavage has been observed when the complexes are in the presence of OH and water, under which conditions the reaction is favored by the formation of P−OH[6] or P=O bonds.[7]

Examples of the latter type of reactivity involving the cleavage of P−C bonds of chelating diphosphines bearing perfluoro aromatic substituents,[8]as well as those in which the

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* To whom correspondence should be addressed. E-mail: juvent@servidor.unam.mx.

[†] Universidad Nacional Autónoma de México.

[‡] University of Rochester.

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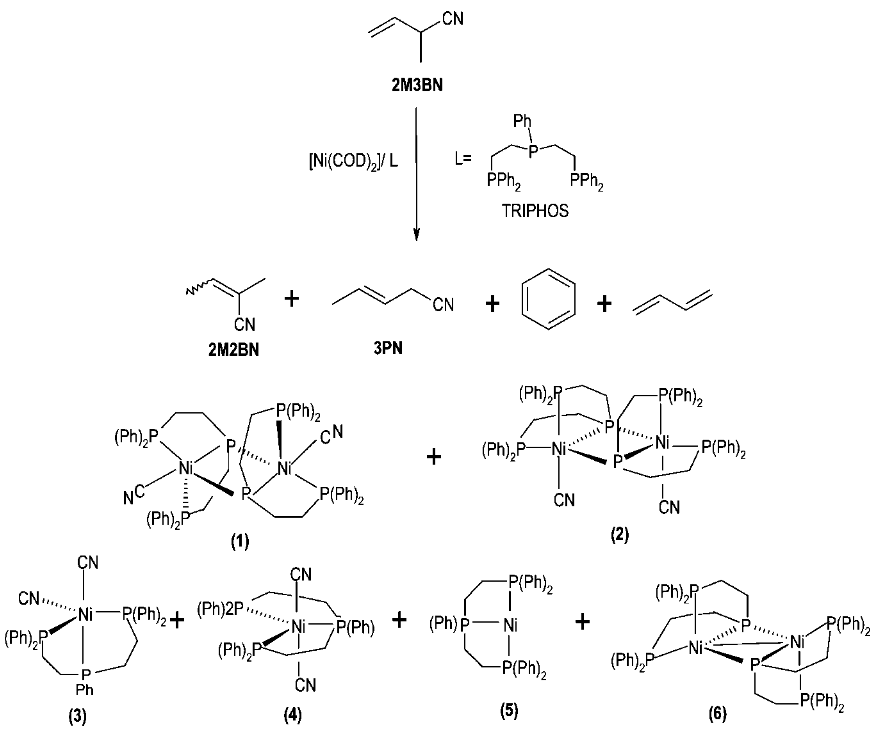
10.1021/om7011425 CCC: $40.75

Scheme 1



cleavage was observed to take place over the bridging hydrocarbon chain, are also known.[9] Reversibility of the P−C bond cleavage reaction in the case of palladium complexes has also been reported.[10] Formation of biphenyls as a consequence of successive P−C bond cleavage and C−C coupling has been documented for aryl phosphines such as PPh_3;[11] the additional presence of hydride sources been observed to promote the formation of benzene.[4b,11a,12] Related to this, compounds bearing CO ligands have been found to favor the formation of benzaldehyde.[11a,13] Also of note, phenyl moieties resulting from the P−C bond scission of PPh_3 have been reported to remain bound to metal centers in a number of cases, displaying η^1-,[3a3e] μ-η^1-,[3f,4b] η^1:η^2-,[3c,3d] and μ-η^2:η^2-coordinations.[14] In the case of carbonyl-substituted compounds, an acyl complex,[3e,3f] and in the case of cluster systems, one example showing the phenyl moiety that remains coupled to a ring-opened thiophene have also been described.[4c]

The chemistry related to phosphido ligands has been widely studied, the latter being useful ligands for the stabilization of single[4d−4f] and multiple metal−metal bonds.[4a,4b] Phosphido ligands are able to act as both bridging and terminal ligands, extremes that have been observed particularly in the case Pt complexes.[15]

Currently, as a result of our growing interest in the C−CN bond activation reactions[16] and the isomerization of cyano olefins using Ni(0) complexes,[17] we have moved to the use of Ni(TRIPHOS) complexes for the isomerization of 2M3BN. We find that contrary to other P-donor ligands already used, the TRIPHOS ligand suffers a P−C bond cleavage that accompanies the additional cleavage of the C−CN bond at the cyanoolefin, both under catalytic and stochiometric conditions. In addition, this catalyst does not show similar selectivity for 3-PN as seen with the commercial catalyst. Details of these studies are presented in this paper.

Results and Discussion

Study of the Isomerization Reaction under Catalytic Conditions. The catalytic isomerization reaction of neat 2M3BN in the presence of $[Ni(COD)_2]$, used as a catalytic precursor, and the TRIPHOS ligand at a 110-fold excess of the substrate and 100 °C, yielded 100% conversion of the substrate producing *Z*- and *E*-2M2BN (57% and 31%, respectively) within 24 h; a poor yield of 3PN (5%) was also observed[18] (see Scheme 1). A crop of air-stable red crystals, namely *trans*-$[Ni_2(\mu\text{-}P(CH_2CH_2PPh_2)_2)_2(CN)_2]$ (**1**), was obtained from the reaction mixture (see the Experimental Section). The crystals were suitable for X-ray diffraction studies, the structure of the latter compound being shown in Figure 1. Relevant crystallographic data for this compound are summarized in Table 1.

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(18) The presence of the nitriles was analyzed by GC-MS and ^1H NMR in toluene-d_8 solution.

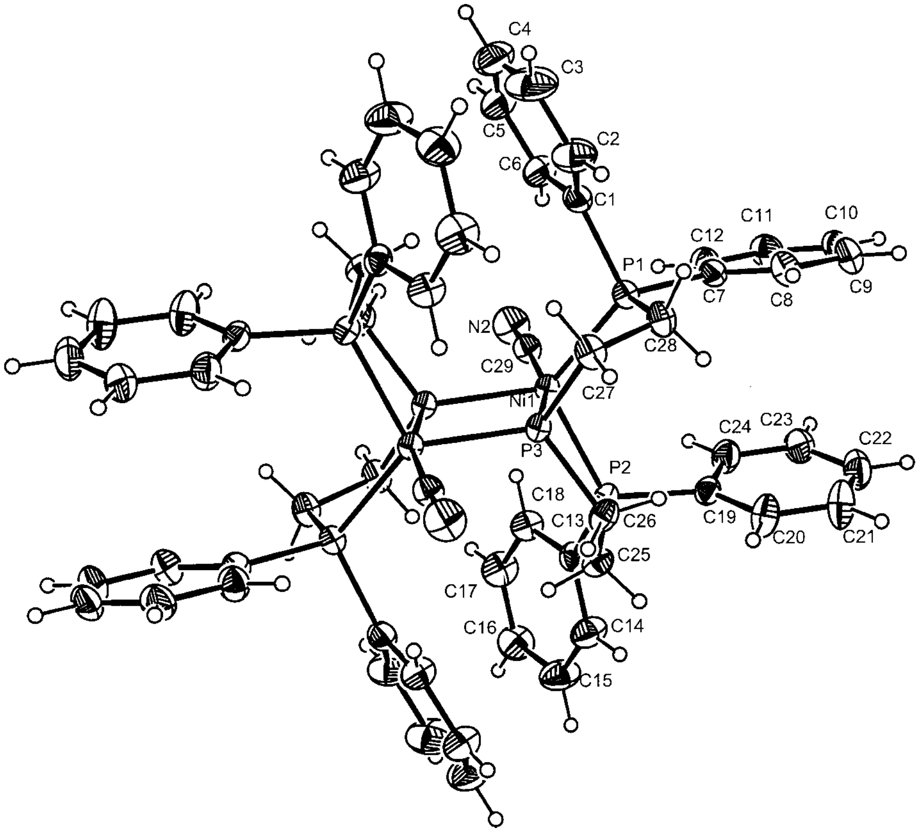

Figure 1. ORTEP drawing of complex **1** at 50% probability. Selected bond distances (Å): Ni1−P1 (2.2063(7)), Ni1−P2 (2.2452(6)), Ni1−P3 (2.2018(6)), Ni2−P3 (2.1987(6)), Ni1−C29 (1.885(2)), C29−N2 (1.154(3)). Selected angles (deg): P1−Ni−C29 (97.34(8)), P2−Ni−C29 (102.17(8)), P3−Ni−C29 (164.62(8)), P1−Ni−P2 (114.10(2)), P2−Ni−P3 (88.56(2)).

Table 1. Summary of Crystallographic Results for 1 and 3

	1	**3**
empirical formula	$C_{58}H_{56}N_2Ni_2P_6$	$C_{36}H_{33}N_2NiP_3$
fw	1084.29	645.26
temp	298(2) K	298(2) K
wavelength	0.71073 Å	0.71073 Å
cryst system	*P*2(1)/*n*	*P*2(1)2(1)2(1)
space group	monoclinic	orthorhombic
unit cell dimensions	a = 12.9870(13) Å, α = 90°	a = 7.6630(18) Å, α = 90°
	b = 14.4380(14) Å, β= 92.250(8)°	b = 19.375(5) Å, β = 90°
	c = 13.7690(11) Å, γ=90° γ = 90°	c = 21.757(7) Å, γ = 90°
volume	2579.8(4) $Å^3$	3230.3(15) $Å^3$
Z	2	4
density (calcd)	1.396 Mg/m^3	1.327 Mg/m^3
abs coeff	0.957 mm^{-1}	0.777 mm^{-1}
F(000)	1128	1344
crystal size	0.6 × 0.6 × 0.53 mm^3	0.3 × 0.2 × 0.1 mm^3
θ range for data collection	2.04 to 25.99°	1.41 to 27.99°
index ranges	$-1 \le h \le 16, -1 \le k \le 17, -16 \le l \le 16$	$-1 \le h \le 10, -1 \le k \le 25, -1 \le l \le 28$
no. of reflns collected	6200	5523
no. of independent reflns	5041 [*R*(int) = 0.0199]	5268 [*R*(int) = 0.0262]
completeness to θ	99.8% (25.99°)	100% (27.99°)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	5041/0/259	5268/0/379
goodness-of-fit on F^2	1.056	1.035
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0344, *w*R2 = 0.0897	R1 = 0.0482, *w*R2 = 0.0925
R indices (all data)	R1 = 0.0430, *w*R2 = 0.0935	R1 = 0.0797, *w*R2 = 0.1051
largest diff peak and hole	0.565 and –0.233 e·$Å^{-3}$	0.294 and –0.257 e·$Å^{-3}$

The structure of complex **1** can be envisaged as the result of a P—C bond cleavage of the TRIPHOS ligand, losing the phenyl group attached to the central phosphorus atom of the tridentate ligand, thereby resulting in the formation of a binuclear compound with a phosphido bridge. The structure of this compound also displays two CN ligands, one coordinated to each metal center. As such, they provide evidence for C—CN bond cleavage taking place in the substrate, 2M3BN. Each nickel center shows a distorted trigonal bipyramidal geometry, where the apical positions are occupied by −CN and phosphido moieties, the equatorial positions around each metal center being occupied by PPh_2 and a second phosphido moiety. The Ni—P bond distances in the phosphido bridge complex **1**are 2.2018(6) and 2.1987(6)

Å, which are slightly longer than those observed in the related compound [(η^5-Cp)Ni(μ-CO)(μ-PMe$_2$)(η^5-Cp)W(Me)(PMe$_3$)], 2.114(2) Å.

The reaction mixture was analyzed by GC-MS and, in addition to the isomerized nitriles described above, a significant amount of benzene and butadiene were also confirmed to be present after 24 h reflux. Our interpretation of the transformations that take place is summarized in Scheme 1. The ^{31}P{^{1}H} NMR spectrum of an aliquot of the reaction mixture in CDCl$_3$ displayed a number of different signals, those for complex **1** being observed at 44.1 ppm (dd, $^{2}J_{P-P}$ = 48.0 and 38.5 Hz), assigned to the phosphido bridge, and an additional pair of doublets at 54.8 ($^{2}J_{P-P}$ = 48.0 Hz) and 23.8 ppm ($^{2}J_{P-P}$ = 38.5 Hz) for the PPh$_2$ moieties. A similar set of minor signals was observed at 53.1 (dd, $^{2}J_{P-P}$ = 53.7 and 32.1 Hz), 50.2 (d, $^{2}J_{P-P}$ = 53.7 Hz), and 25.3 ppm (d, $^{2}J_{P-P}$ = 32.1 Hz). The two sets of signals were attributed to the presence of two isomers, namely the trans- and cis-isomers of [Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$(CN)$_2$], compounds **1** and **2**, respectively (Scheme 1). Additional species present in the crude reaction mixture, compounds **3**−**6** (vide infra), could also be isolated and characterized further upon workup. Evaporation of solvent followed by extraction with THF left behind a red residue, whose ^{31}P{^{1}H} NMR spectrum in CDCl$_3$ showed the presence of two isomers in a 7:1 ratio, assigned as *cis*- and *trans*-[Ni(TRIPHOS)(CN)$_2$] (**3** and **4**). Of these, the compound in the higher proportion, complex **3**, displayed a doublet centered at 37.9 ppm ($^{2}J_{P-P}$ = 29.3 Hz) and a broad triplet at 98.4 ppm ($^{2}J_{P-P}$ = 29.3 Hz), while the second compound, complex **4**, showed a doublet at 39.5 ppm ($^{2}J_{P-P}$ = 30.1 Hz) and a triplet at 103.5 ppm ($^{2}J_{P-P}$ = 30.1 Hz). The coupling constants for such species are consistent with those of Ni(II) complexes. The ^{1}H NMR spectrum of the same pair of species displayed a multiplet between 6.97 and 7.9 ppm (25H) for the aromatic protons of the TRIPHOS ligand and a multiplet centered at 2.36 ppm (8H) for the methylene groups within the same ligand. The ^{13}C{^{1}H} NMR spectrum displayed two multiplets at 28.0 and 29.4 ppm that were assigned to the methylene carbons of the major species, **3**, and two other multiplets at 25.8 and 33.4 ppm for the minor species, **4**. The aromatic carbons appeared as overlapping multiplets between 128.7 and 134.7 ppm. The resonance for the −CN ligand appeared overlapped with those of the aromatic signals; however, the IR allowed us to confirm the presence of such ligand at 2199 and 2095 cm^{-1}.

Suitable crystals for X-ray diffraction studies of complex **3** were obtained by vapor diffusion of a THF/CH$_2$Cl$_2$ system. The molecular structure of complex **3** is depicted in Figure 2, and a summary of the relevant crystallographic data for this compound is included in Table 1. The geometry around the Ni center in **3** is trigonal bipyramidal with the cyanide ligands occupying both axial and equatorial positions. The P—Ni bond distances of 2.1932(4), 2.2149(14), and 2.2425(13) Å, for the chelate are similar to those found in closely related compounds such as [Ni(TRIPHOS)(η^3-C$_3$H$_3$)]$^+$:[19] 2.2463(13), 2.2475(13), and 2.2501(12) Å; the Ni—CN bond distances in compound **3** are in agreement with those found in other compounds of nickel(II).[16a]

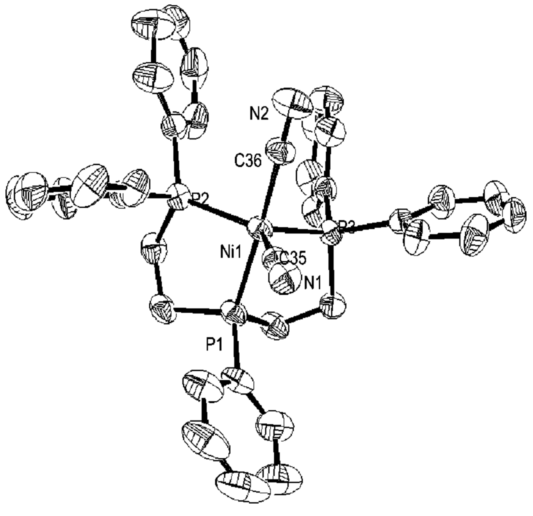

Figure 2. ORTEP drawing of complex **3** at 50% probability. Selected bond distances (Å): Ni1−P1 (2.1932(14)), Ni1−P2 (2.2149(14)), Ni1−P3 (2.2425(13)), Ni1−C35 (1.947(5)), Ni1−C36 (1.894(5)). Selected angles (deg): P1−Ni1−P2 (85.77(6)), P2−Ni1−P3 (120.01(5)), P3−Ni1−P1 (87.53(5)), P1−Ni1−C35 (94.14(13)), P1−Ni1−C36 (176.53(16)), P2−Ni1−C35 (123.89(14)), P2−Ni1−C36 (91.20(16)).

After having separated compounds **3** and **4** from the reaction mixture the remaining mother liquors produced two more compounds following chromatography, tentatively assigned on the basis of spectroscopic and reactivity data as [Ni(TRIPHOS)] (**5**) (still containing traces of **2**) and [Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$] (**6**). The ^{31}P{^{1}H} NMR for the less polar fraction, complex **5** (Scheme 1), displayed a doublet at 45.9 ppm ($^{2}J_{P-P}$ = 48.5 Hz) and a triplet at 108.3 ppm ($^{2}J_{P-P}$ = 48.5 Hz). The ^{1}H NMR spectrum of this compound showed several signals between 1.6 and 3.07 ppm (8H) and a broad multiplet for the aromatic protons between 6.9 and 8.6 ppm (25H). The ^{13}C{^{1}H} NMR spectra displayed multiplets for the methylene carbons at 25.3 and 28.3 ppm only; the aromatic carbons were detected in the range of 125–134.7 ppm. No signals in either the ^{13}C{^{1}H} NMR or the IR spectrum of this compound were found for a −CN ligand, suggesting the presence of a vacant site as proposed for compound **5**. Additional evidence for this formulation comes from the addition of PPh$_3$, which produces the known complex [Ni(TRIPHOS)(PPh$_3$)].[20]

The more polar fraction containing complex **6** displayed a doublet centered at 28.5 ppm, ($^{2}J_{P-P}$ = 51.7 Hz, *P*Ph$_2$) and a triplet centered at 37.8 ppm ($^{2}J_{P-P}$ = 51.7 Hz, *μ-P*) in the ^{31}P{^{1}H} NMR spectrum. The pattern is consistent with that of a phosphido bridge compound as in the case of **1**, and thus it was assigned as having the formulation [Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$]. A related dimeric compound [Ni$_2$(μ-PCy$_2$)$_2$(PCy$_2$Me)$_2$] with similar chemical shift and multiplicity assigned to the resonance for the phosphido bridge is in agreement with the proposed structure (δ 23.6).[21] The ^{1}H NMR spectrum for compound **6** displayed two broad signals at δ 2.30 and 2.07 ppm (8H) for the methylene protons and a multiplet centered at 7.54 ppm for the aromatic protons. The ^{13}C{^{1}H} NMR spectrum of **6** showed resonances for the methylene groups as doublets of doublets at δ 22.4 (dd, $^{1}J_{C-P}$ = 66.5 and $^{2}J_{C-P}$ = 4.0 Hz) and δ 21.5 (dd, $^{1}J_{C-P}$ = 70.2 and $^{2}J_{C-P}$ = 4.3 Hz); the aromatic carbons appeared between 129.1 and 133.9 ppm. Again, no signals either in the ^{13}C{^{1}H} NMR or IR spectrum of the compound were found for potential −CN moieties, and therefore a structure lacking such entities, as depicted in Scheme 1, was proposed.

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Study of the Isomerization Reaction under Stoichiometric Conditions. After having established the distribution of products under catalytic conditions, the isomerization reaction of 2M3BN was studied under stoichiometric conditions. This particular reaction was carried out with THF or THF-d_8 at 100 °C. The formation of the organic products *E*- and *Z*-2M2BN, along with a small amount of 3PN and benzene, as in the catalytic case, was detected by GC-MS. Examination of the ^{1}H NMR of the mixture confirmed in addition the presence of 1,3-butadiene. The production of complexes **2**, **5**, and **6** was also established by means of $^{31}P\{^1H\}$ NMR spectroscopy of the same mixture, dissolved in THF-d_8.

Remarkably, a catalytic run with **3** as catalytic precursor was carried out to establish its participation in the P—C bond cleavage reaction that is related to the formation of benzene. Only cyanoolefins (*Z*-2M2BN (77%), *E*-2M2BN (15%), and *cis*-2PN (8%)) were detected from this experiment by means of GC-MS at the end of the reaction and as a result, we have speculated on a possible mechanistic pathway (see Scheme 2). We propose the isomerization reaction of 2M3BN into 2M2BN to occur initially by the formation of [Ni(TRIPHOS)(η^2-*C*,*C*-2M3BN)] (**A**), followed by the formation of a nickel(II) allyl—hydride complex (**B**), which promotes a C—H bond breaking/forming step and evolves into a rearranged alkene complex (**C**). This is thought to be followed by the release of the isomerized olefin with the concurrent formation of complex **5**. Additionally, **A** can participate in a C—CN breaking/forming catalytic cycle, from which the isomerization of 2M3BN to the linear 3PN, through the formation of a nickel(II) allyl—cyanide complex (**D**), can also take place. At this point, β-elimination can occur to yield 1,3-butadiene, producing a Ni(II)-hydride—cyanide complex as well. The latter hydride intermediate is likely involved in the P—C bond scission of the TRIPHOS ligand that precedes the formation of benzene. The cleavage can take place by at least two pathways involving a hydride transfer:[2a] the first leading to the formation of compounds **1** and **2** and the second to compound **6**, along with **3** or **4**.

Conclusions

The reactivity of "Ni(TRIPHOS)" complexes with 2M3BN yields C—H bond activation products that promote the formation of the stable branched isomers *E*- and *Z*-2M2BN, along with C—CN activation products that enable the formation of 3PN, although only in low yields. The low yields for the linear 3PN are attributed to the occurrence of C—P bond cleavage reactions taking place over the TRIPHOS ligand that result in the formation of very stable μ-phosphide nickel dinuclear complexes that deactivate the catalytic process.

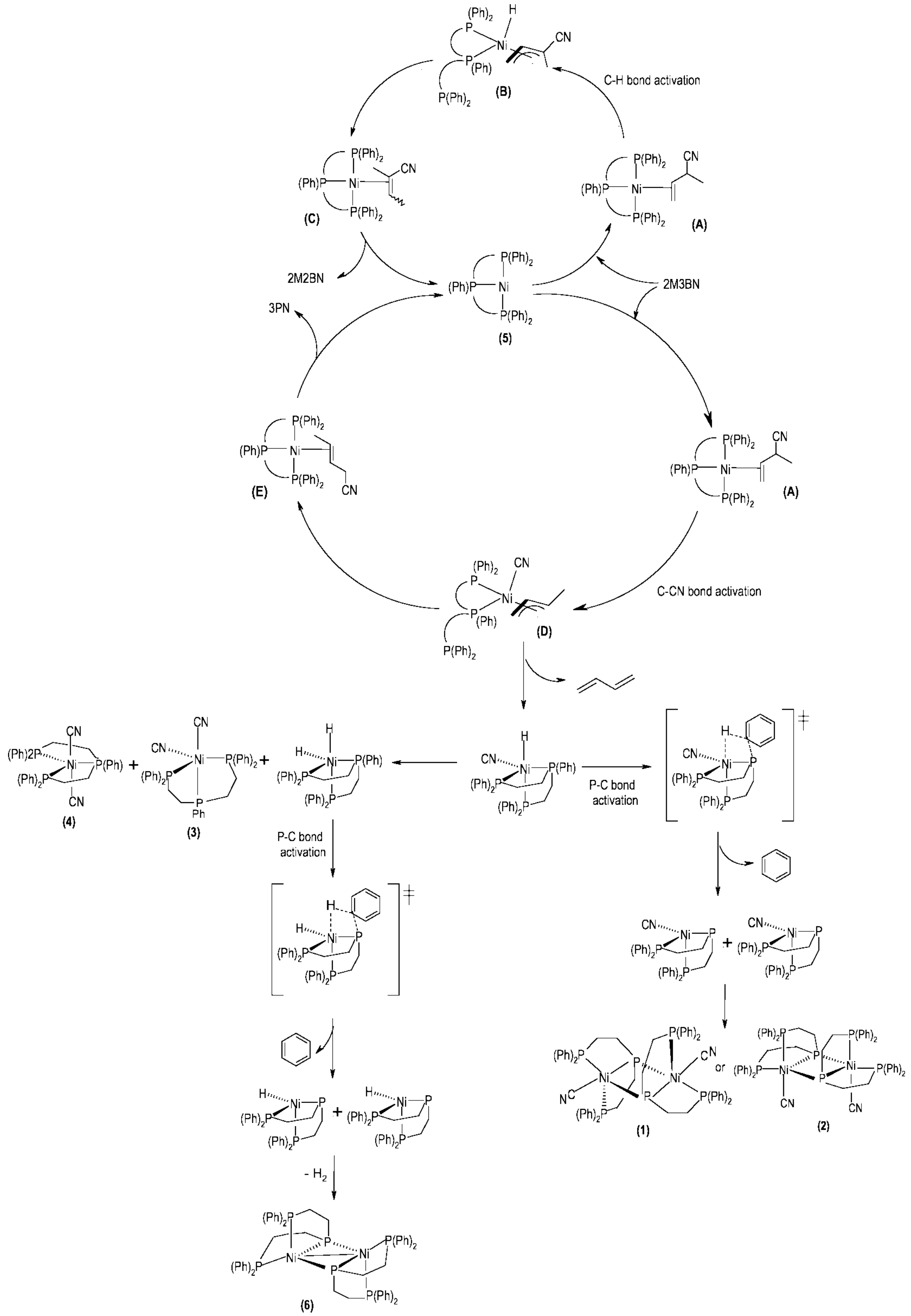
Experimental Section

All manipulations were carried out with standard Schlenk and glovebox techniques under argon (Praxair 99.998). THF and hexane (J. T. Baker) were dried and distilled from sodium/benzophenone ketyl solutions. Ethanol (J. T. Baker) was dried over 3Å molecular sieves and deoxygenated with argon. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3Å molecular sieves in an MBraun glovebox (<1 ppm H_2O and O_2). [Ni(COD)$_2$] was purchased from Strem and purified from a THF solution, filtered through Celite, and vaccuum dried to yield yellow crystalline [Ni(COD)$_2$], which was further dried for 3 h in vacuo. TRIPHOS was purchased from Strem and was used as received. 2M3BN (86.5% by GC-MS) was purchased from TCI America, purged, and stored in the glovebox. ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in $CDCl_3$. ^{1}H chemical shifts (δ) are reported relative to the residual proton resonances in the deuterated solvent. $^{13}C\{^1H\}$ NMR chemical shifts (δ) are reported relative to resonance of the deuterated solvent. All $^{31}P\{^1H\}$ NMR spectra were recorded relative to external 85% H_3PO_4. All NMR spectra and catalytic reactions were carried out with thin wall (0.38 mm) WILMAD NMR tubes with J. Young valves. A Siemens P4 four-cycle diffractometer at room temperature with monochromatized Mo Kα radiation (λ = 0.71073 Å) was used for the X-ray structure determinations. Infrared spectra were obtained on a Perkin-Elmer 1600 FT spectrophotometer. Elemental analyses were carried out by USAI-UNAM, using an EA 1108 FISONS Instrument analyzer. Reproducible elemental analyses could not be obtained for complexes **5** and **6** due to the high air sensitivity of these samples (they are Ni^0). Mass determinations were made on a JEOL SX-102A (FAB+), using nitrobenzilic alcohol matrix and GC-MS determinations on a Varian Saturn 3 with a 30 m DB-5MS capillary column.

Catalytic Isomerization of 2M3BN. A suspension of 2M3BN (0.4 mL, 4.00 mmol) and TRIPHOS (19.2 mg, 0.036 mmol) was added to crystalline [Ni(COD)$_2$] (10 mg, 0.036 mmol), which rendered an orange suspension after 15 min of stirring. The mixture was transferred to an NMR tube with a J. Young valve and the tube was heated at 100 °C in an oil bath with stirring, producing a red solution. After cooling to room temperature, a sample of the reaction mixture was taken and dissolved in THF inside the drybox and analyzed by GC-MS. A second sample was dissolved in toluene-d_8 and analyzed by ^{1}H NMR spectroscopy. The latter sample displayed resonances characteristic of *E*- and *Z*-2M2BN and *trans*-3PN. The use of catalytic amounts of **5** gave similar activity.

Preparation of *cis*- and *trans*-[Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$(CN)$_2$] (1, 2), *cis*- and *trans*-[Ni(TRIPHOS)(CN)$_2$] (3, 4), [Ni(TRIPHOS)] (5), and [Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$] (6). A suspension of 2M3BN (1.6 mL, 16.0 mmol) and TRIPHOS (76.8 mg, 0.144 mmol) was added to yellow crystalline [Ni(COD)$_2$] (40 mg, 0.144 mmol), which after 15 min of stirring produced an orange suspension. The mixture was transferred to an NMR tube with a J. Young valve, and the tube was heated at 100 °C in an oil bath with stirring during 24 h. After this time, complex **1** precipitated as a red crystalline solid, and was filtered out and dried in vacuo for 3 h. The filtrate was evaporated to dryness and dried in vacuo for 3 h. The residue was washed with THF leaving behind a mixture of complexes **3** and **4** as a red powder, which were filtered and further dried in vacuo. The mother liquors were then reduced in volume and separated by column chromatography on silica gel, eluting first with hexane and then increasing the polarity to hexane/ethanol 1:1 (v/v). The less polar fraction contained mainly complex **5** (yellow powder containing traces of **2**) and the more polar fraction contained complex **6** (dark brown). The spectroscopic and analytical details are as follows: *trans*-[Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$(CN)$_2$] (**1**): 10 mg, 13% (isolated). Anal. Calcd for $C_{58}H_{56}N_2Ni_2P_6$: C 64.20, H 5.16, N 2.58. Found (crystals): C 64.10, H 5.13, N 2.50. MS-FAB+ = 1084 (M$^+$). ^{1}H NMR (299.7 MHz): δ 2.5 (m, 8H, CH_2), 6.91–7.8 (m, 25H, aromatic). $^{13}C\{^1H\}$ NMR: δ 135.6–128.2 (CN and aromatic carbons), 27.2 and 24.4 (CH$_2$P). $^{31}P\{^1H\}$ NMR (121.3 MHz): δ 54.8 (d, $^2J_{P-P}$ = 48.0 Hz, P(Ph)$_2$R), 44.1 (dd, $^2J_{P-P}$ = 48.0 and 38.5 Hz, phosphido bridge), 23.8 (d, $^2J_{P-P}$= 38.5, P(Ph)$_2$R). IR: ν = 2108 cm^{-1}, —CN. *cis*-[Ni$_2$(μ-P(CH$_2$CH$_2$PPh$_2$)$_2$)$_2$(CN)$_2$] (**2**): $^{31}P\{^1H\}$ NMR (121.3 MHz): δ 53.1 (dd, $^2J_{P-P}$= 53.7 and 32.1 Hz, phosphido bridge), 50.2 (d, $^2J_{P-P}$= 50.2 Hz, P(Ph)$_2$R), 25.2 ppm (d, $^2J_{P-P}$= 32.1 Hz, P(Ph)$_2$R). *cis*- and *trans*-[Ni(TRIPHOS)(CN)$_2$] (**3** and **4,** respectively): 30.2 mg, 32.5% (isolated). Anal. Calcd for $C_{36}H_{33}N_2NiP_3$: C 66.97, H 5.12, N

Scheme 2



4.34. Found: C 68.14, H 5.28, N 4.08. MS-FAB+ = 645 (M^+), 620 (M^+ − CN). ^{1}H NMR (299.7 MHz): δ 2.36 (m, 8H, CH_2), 6.97–7.9 (m, 25H, aromatic). ^{13}C{^{1}H} NMR (75.4 MHz): δ 134.7–128.7 (multiplets, aromatic carbons), 33.4–25.8 (m, CH_2, one isomer), 29.4–28.0 (m, CH_2 one isomer) . ^{31}P{^{1}H} NMR (121.3 MHz): δ 103.5 (t, $^2J_{P-P}$= 30.1 Hz), 98.4 (t, $^2J_{P-P}$= 29.3 Hz), 39.5 (d, $^2J_{P-P}$= 30.1 Hz), 37.9 (d, $^2J_{P-P}$= 29.3 Hz). IR: ν = 2199 and 2095 cm^{-1}, −CN. **[Ni(TRIPHOS)] (5):** 16 mg, 18.5%. FAB+: 597 (M^+), the air sensitivity of the sample and presence of traces of **2** did not allow reproducible elemental analysis. ^{1}H NMR (299.7 MHz): δ 8.6–6.9 (m, 25H, aromatic protons), several multiplets at 3.07–3.01, 2.89–2.8, 2.7–2.55, 2.4–2.27, 2.17–2.00, 1.87–1.6 (8H for all, CH_2). ^{13}C{^{1}H} NMR (75.4 MHz): δ 134.7–125 (aromatic carbons), 28.3 (m, CH_2), 25.3 (m, CH_2). ^{31}P{^{1}H} NMR (121.3 MHz) δ 108. 3 (t, $^2J_{P-P}$= 48.5 Hz), 45.9 (d, $^2J_{P-P}$= 48.5 Hz). The addition of PPh_3 gave the same spectra as reported for [Ni(TRIPHOS)PPh_3]. **[Ni_2(μ-P($CH_2CH_2PPh_2$)$_2$)$_2$] (6):** 20 mg, 13.5%. The high air sensitivity of the sample did not allow reproducible elemental analysis. ^{1}H NMR (299.7 MHz): δ 7.54 (m, 20H, aromatic protons), 2.30–2.07 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (75.4 MHz): δ 133.9–129.1 (aromatic carbons), 22.4 (dd, $^1J_{C-P} = 66.5$ and $^2J_{C-P} = 4.0$ Hz, CH_2−P), 21.5 (*d*d, $^1J_{C-P} = 70.2$ and 4.3 Hz, CH_2−P). $^{31}P\{^1H\}$ NMR (121.3 MHz) δ 37.8 (t, $^2J_{P-P}$= 51.7 Hz), 28.5 ppm (d, $^2J_{P-P}$= 51.7 Hz). The reactión of **1** (10 mg) with an excess of sodium allow the formation of the same signals above quoted for **6**.

Acknowledgment. We thank CONACyT (grant 42467-Q) and DGAPA-UNAM (grant IN202907-3) for financial support for this work. A.A.-R. also thanks CONACyT for a graduate studies grant. The authors also thank Dr. A. Arévalo for technical assistance. W.D.J. acknowledges support from the U.S. Department of Energy, grant no. FG02-86ER13569.

Supporting Information Available: Detailed GC-MS determinations and tables of complete crystallographic data for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7011425