Structural Divergence in the Products of the Reaction of [MoCl(η^3-C_3H_5)$(CO)_2$(dmpm)] with Nucleophiles

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Received November 5, 2002

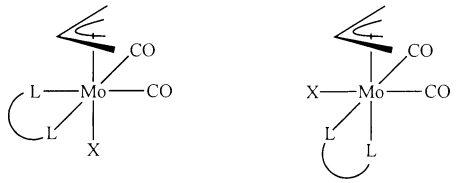
The complex [MoCl(η^3-allyl)$(CO)_2$(dmpm)] (dmpm = bis(dimethylphosphino)methane) (**1**) reacts with sodium azide and with sodium cyanide to afford the new complexes [Mo(N_3)-(η^3-allyl)$(CO)_2$(dmpm)] (**2**) and [Mo(CN)(η^3-allyl)$(CO)_2$(dmpm)] (**3**), respectively, which were characterized spectroscopically and by X-ray diffraction. Complex **2** is a *cis*-dicarbonyl in which one of the P atoms of dmpm is approximately *trans* to a carbonyl, and the other is *trans* to the allyl. In contrast, **3** is a rare *trans*-dicarbonyl. A theoretical analysis was applied to rationalize this difference.

Introduction

The reaction of [MoX(η^3-allyl)$(CO)_2$(L−L)] (X = anionic monodentate ligand, L−L = neutral diimine or diphosphine chelate) complexes with resonance-stabilized carbanions inspired the use of Mo complexes as allylic alkylation catalysts[1] and models a proposed step of this catalytic process.[1,2] There are important differences between the complexes with L−L = bipy or phen and those in which L−L is a chelating diphosphine.[3] Thus, whereas the former are rigid molecules with the allyl and X ocupying mutually *trans* positions (structure A in Chart 1), the latter are fluxional in solution and feature solid state structures with one of the phosphorus donors *trans* to the allyl ligand (structure B in Chart 1).[4]

We have recently isolated stable alkyls and alkynyls [MoR(η^3-allyl)$(CO)_2$(N−N)] (N−N = 2,2′-bipyridine or 1,10-phenanthroline) from the reaction of chloro precursors with nonstabilized carbanions.[5] These products retain the above-mentioned features of the halo precursors, i.e., rigidity in solution and a geometry with mutually *trans* R and allyl groups. As a consequence, these alkyl complexes do not undergo reductive elimination of alkyl−allyl coupling products. In contrast, we found that [MoCl(η^3-allyl)$(CO)_2$(dmpm)] (dmpm = bis-(dimethylphosphino)methane) reacts with acetylide, enolate, or alkyl anions R^- to afford the products of the allyl−anion coupling through the intermediacy of complexes having the R and allyl groups in *cis* positions.[6] In a first step, the R carbanion substitutes the Cl ligand with a retention of the geometry, and, subsequently, the product isomerizes to an unprecedented *trans*-dicarbonyl complex, which is the species that undergoes the elimination of the R−allyl coupling product.

Chart 1



A B

These results and the lack of previous studies in this area led us to investigate the reactivity of [MoCl(η^3-allyl)$(CO)_2$(dmpm)] (**1**) with different anions; our first results are the matter of this paper.

Results and Discussion

The reaction of **1** with sodium azide afforded [Mo(N_3)-(η^3-C_3H_5)$(CO)_2$(dmpm)] (**2**). The IR spectrum of **2** showed two intense C−O bands at 1936 and 1851 cm^{-1}, corresponding to the *cis*-Mo$(CO)_2$ unit, and a strong band at 2072 cm^{-1}, assigned to the azido group. The three-signal pattern for the allyl ligand in ^{1}H NMR, along with the single peak in ^{31}P NMR, is consistent with fluxional behavior, as is typical of [MoX(η^3-allyl)$(CO)_2$(P−P)] species (see above), given that the molecule of **2** lacks

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10.1021/om020919m CCC: $25.00
Publication on Web 02/27/2003

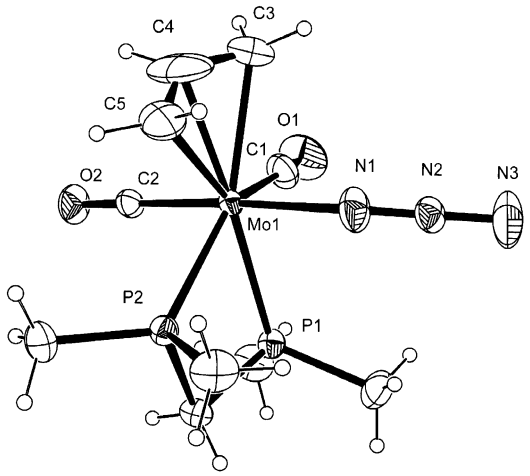

Figure 1. Thermal ellipsoid (30%) plot of complex **2**. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) 2.270(4), Mo(1)−P(1) 2.4702(12), Mo(1)−P(2) 2.4795(10), N(1)−N(2) 1.128(5), N(2)−N(3) 1.156(5), C(2)−Mo(1)−N(1) 175.14(15), C(1)−Mo(1)−N(1) 101.22(17), N(2)−N(1)−Mo(1) 135.4(3), N(1)−N(2)−N(3) 176.8(5).

any elements of symmetry, as shown by the results of an X-ray structural determination (Figure 1).

The molecule of **2** shows the geometry typically found for [MoX(η^3-allyl)(CO)$_2$(P−P)] complexes, i.e., P atoms *trans* to the allyl group and to one CO. However, the allyl group of **2** is oriented *endo*, with the open face opposed to the carbonyls.[7] The normal (*exo*) allyl orientation, with the allyl open face pointing toward the carbonyls, was found in the [MoX(η^3-allyl)(CO)$_2$(L−L)] compounds that have been structurally characterized so far and was found to be favored for these pseudo-octahedral compounds on the basis of EHMO calculations.[8] On the other hand, the *endo* orientation, as in **2**, has been found only in complexes with cyclopentadienyl[9] or tris(pyrazolyl)borato[10] (Tp) ligands occupying the coordination positions of X and dmpm ligands in our complexes.

Compound **1** reacted with NaCN to give [Mo(CN)(η^3-C_3H_5)(CO)$_2$(dmpm)] (**3**). The most striking structural feature of **3** is the mutually *trans* disposition of the two CO ligands, indicated by a single ν_{CO} band at 1867 cm^{-1} and by the two ^{13}C NMR carbonyl signals (a single ν_{CO} band could also be consistent with the presence of a single CO ligand). A weak IR band at 2069 cm^{-1} was assigned to the ν_{CN} stretch of the cyanide ligand. Unlike previously known [MoX(η^3-allyl)(CO)$_2$(P−P)] compounds, **3** is stereochemically rigid in solution at room temperature, and the structure deduced from the spectroscopic data in solution coincides with that present in the solid state, which was determined by X-ray diffraction (Figure 2). Thus, the OC−Mo−CO angle is 174.1(3)°. A *trans* M(CO)$_2$ arrangement in dicarbonyl complexes is electronically disfavored because competition for the back-donation of the metal electron density is maximized between mutually *trans* ligands; hence, strongly π-acceptor CO ligands prefer to be *trans* to ligands other than CO.[11] As a result, *trans*-dicarbonyls are very rare and, among the plethora of Mo(II) complexes, virtually unprecedented. Considering together the structures of **2** and **3**, it seems that the *trans* geometry of **3** is due to the electronic properties of the CN ligand (a cyanocomplex isostructural with **2** would not present additional steric hindrance compared with these compounds). It is noteworthy that some of the few other *trans*-dicarbonyl complexes also possess cyano ligands.[12]

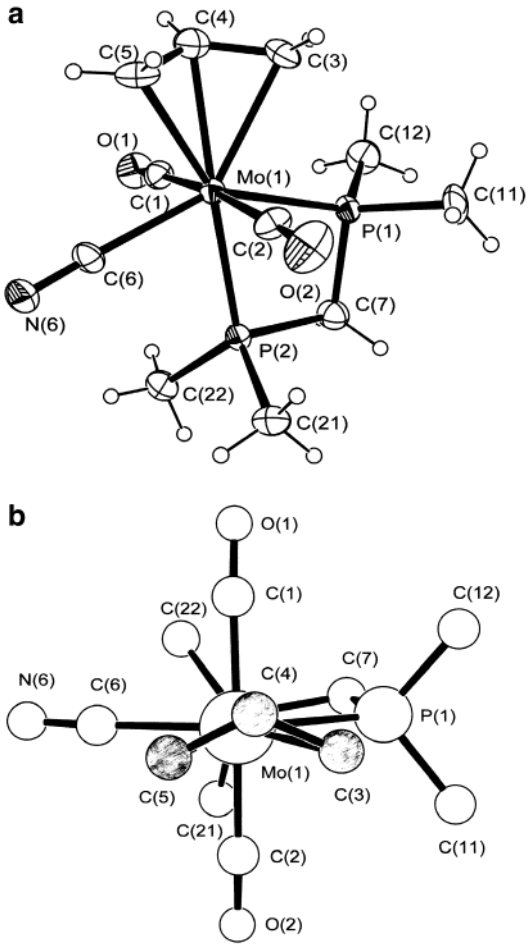

Figure 2. Thermal ellipsoid (30%) plot of complex **3**. Selected bond lengths (Å) and angles (deg): Mo(1)−C(6) 2.255(9), Mo(1)−P(2) 2.501(3), Mo(1)−P(1) 2.504(2), C(6)−N(6) 1.172(11), N(6)−C(6)−Mo(1) 176.5(8).

Also remarkable is that, whereas malonate-type anions attack the allyl group of [MoX(η^3-allyl)(CO)$_2$(L−L)] complexes,[1,13] the reactions of **1** with azide and with cyanide give a single product resulting from chloride substitution in each case, which, despite the mutually *cis* disposition of the η^3-C_3H_5 group and the ligand resulting from the incoming nucleophile, does not undergo coupling.

The orientation of the allyl ligand in **3**, displayed in Figure 2b,[14] deprives the molecule of **3** of a mirror plane,

(7) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.
(8) The angle between the vectors (centroid of Mo(CO)$_2$−Mo) and allyl central carbon−(centroid of the allyl) have been used to specify the rotational orientation of η^3-allyl ligands:[9] These angles are 41(1)° and 19.7(5)° for **2** and **3**, respectively.
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(13) Tom Dieck, H.; Friedel, H. *J. Organomet. Chem.* **1968**, *14*, 375.
(14) In Figure 2b, obtained by spatial rotation of 2a, a ball-and-stick representation was used for clarity.

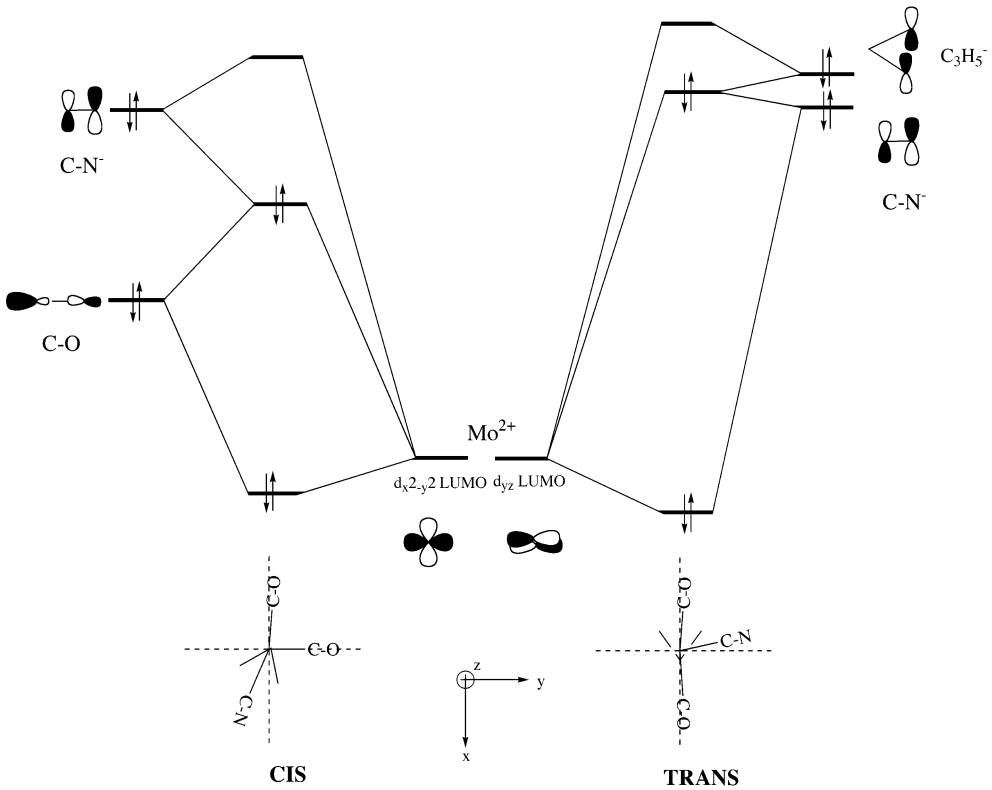

Figure 3. Main orbital interactions diagram for [Mo(CN)(η^3-C_3H_5)$(CO)_2$(dmpm)] (**3**).

Table 1. Crystal Data and Refinement Details for Complexes 2 and 3

	2	**3**
formula	$C_{10}H_{19}MoN_3O_2P_2$	$C_{11}H_{19}MoNO_2P_2$
fw	371.16	353.16
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
a, Å	7.723(2)	8.706(5)
b, Å	14.189(3)	13.546(5)
c, Å	14.656(6)	14.246(5)
α, deg	90	90
β, deg	101.20(3)	101.17(5)
γ, deg	90	90
V, Å^3	1575.5(9)	1648.2(13)
Z	4	4
T, K	293(2)	293(2)
D_c, g cm^{-3}	1.565	1.423
F(000)	752	716
λ(Mo Kα), Å	0.71073	0.71073
cryst size, mm	0.50 × 0.25 × 0.1	0.20 × 0.20 × 0.03
μ, mm^{-1}	1.033	8.254
scan range, deg	2.02 ≤ *θ* ≤ 25.97	4.55 ≤ *θ* ≤ 66.47
abs corr	SADABS	SADABS
no. of reflns measd	3210	2494
no. of ind reflns	3089	2494
no. of data/restraints/ params	3089/0/224	2494/0/173
goodness-of-fit on F^2	1.052	1.005
R_1/R_{w2} [$I>2\sigma(I)$]	0.0290/0.0730	0.00802/0.1988
R_1/R_{w2} (all data)	0.0524/0.0839	0.0920/0.2035

thus making the two CO ligands and the halves of the allyl group inequivalent, as indicated by the ^{1}H and ^{13}C spectra. This allyl orientation can be rationalized using simple MO arguments.[15] Figure 3 displays the main interactions between the fragment {Mo(CN)$(CO)_2$-(dmpm)} and the allyl ligand. Metal orbitals were derived from d^4-ML_5 FMOs [16] by considering the presence of two mutually *trans* CO groups and one CN$^-$ ligand. The strongest bonding combination was that of the π_2 allyl MO with the LUMO of the metal fragment. Additionally, a minor stabilization was produced due to the back-donation from the d_{xy} metal orbital to the π_3 allyl antibonding combination. The maximum overlap between these FMOs was attained when the relative orientation of the allyl ligand and the OC−Mo−CO vector is the one found in **3**.

Whereas this simple picture seems appropriate to rationalize the allyl orientation in **3**, we have performed DFT calculations in an attempt to obtain information on the factors governing the different structures found for **2** and **3**.

B3LYP calculations using the LANL2DZ and LANL1DZ basis sets for Mo and P atoms, respectively, and the 3-21G basis set for C, N, O, and H atoms render the *trans* isomer of [Mo(CN)(η^3-C_3H_5)$(CO)_2$(dmpm)] (with a rotational allyl orientation qualitatively in agreement with the previously mentioned EHMO arguments) 3.01 kcal/mol more stable than the *cis* one in Gibbs energy in solution.[17] Parallel calculations showed *cis*-[Mo(N_3)(η^3-C_3H_5)$(CO)_2$(dmpm)] to be 0.45 kcal/mol more stable than the *trans* isomer. Optimized geom-

(15) EH calculations have been carried out with the model *trans*-[Mo(CN)$(C_3H_5)(CO)_2(PH_3)_2$]. Details available from Prof. A. Galindo (galindo@us.es).

(16) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(17) Calculations were performed with the Gaussian 98 series of programs including the effect of dichloromethane as solvent by means of the PCM method (ϵ = 8.93): Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

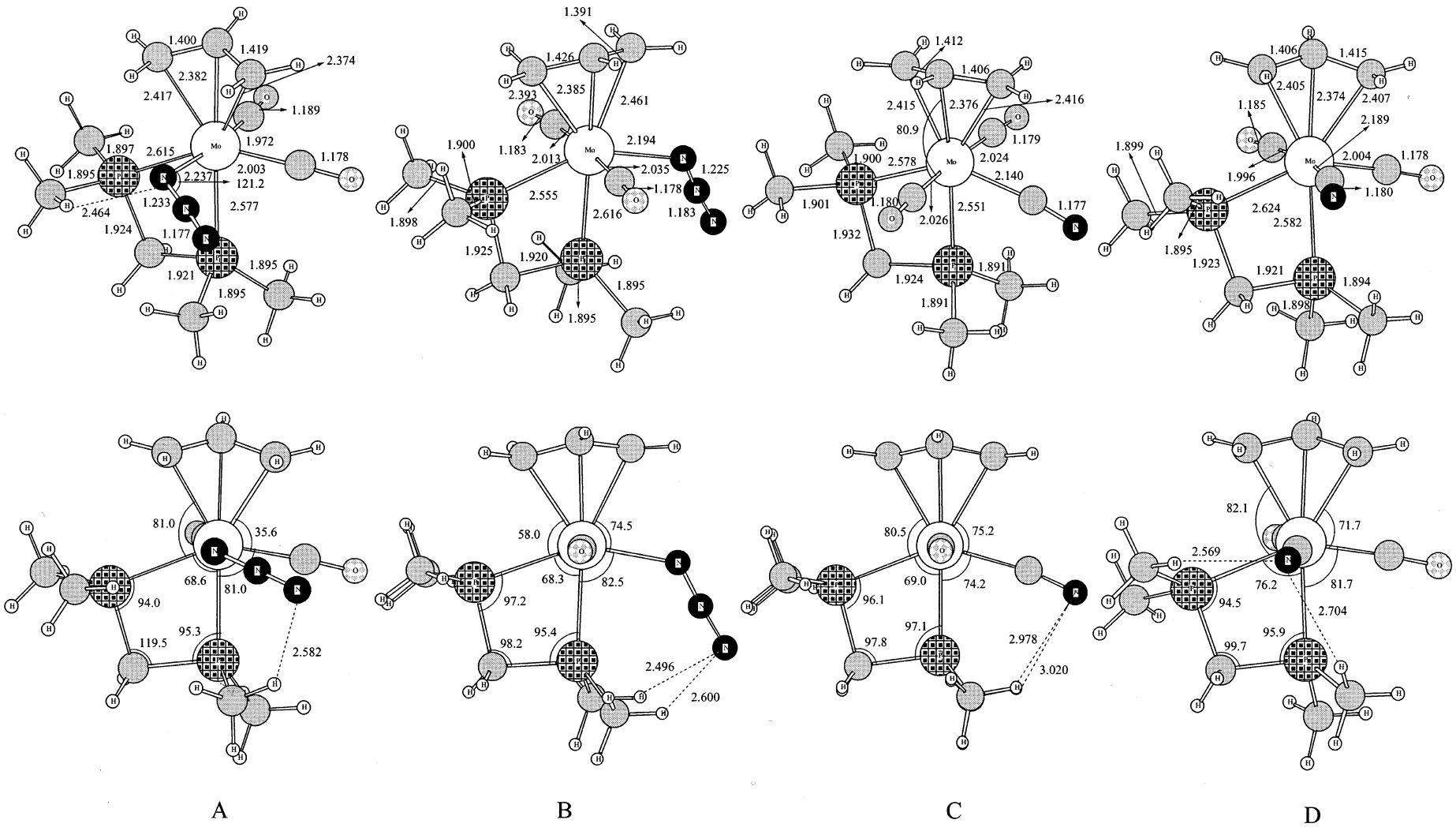

Figure 4. Optimized geometries of (A) *trans*-[Mo(N$_3$)(η^3-C$_3$H$_5$)(CO)$_2$(dmpm)], (B) *cis*-[Mo(N$_3$)(η^3-C$_3$H$_5$)(CO)$_2$(dmpm)], (C) *trans*-[Mo(CN)(η^3-C$_3$H$_5$)(CO)$_2$(dmpm)], and (D) *cis*-[Mo(CN)(η^3-C$_3$H$_5$)(CO)$_2$(dmpm)].

Table 2. B3LYP Calculations for 2 and 3 Using the LANL2DZ and LANL1DZ Basis Sets for Mo and P Atoms, Respectively, and the 3-21G Basis Set for C, N, O, and H Atoms[a]

isomer	ΔE_0	ΔE_{ZPVE}	ΔH	$-T\Delta S$	$\Delta G_{gas-phase}$	$\Delta\Delta G_{solvation}$	$\Delta G_{solution}$
			[Mo(CN)(η^3-C_3H_5)(CO)$_2$(dmpm)] (**3**)				
trans	0.00	0.00	0.00	0.00	0.00	0.0	0.00
cis	1.63	0.36	1.86	0.47	2.33	0.68	3.01
			[Mo(N_3)(η^3-C_3H_5)(CO)$_2$(dmpm)] (**2**)				
cis	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans	1.61	−0.16	1.43	0.14	1.57	−1.12	0.45

[a] The effect of dichloromethane as solvent was included by the PCM method ($\epsilon = 8.93$). Energies in kcal/mol.

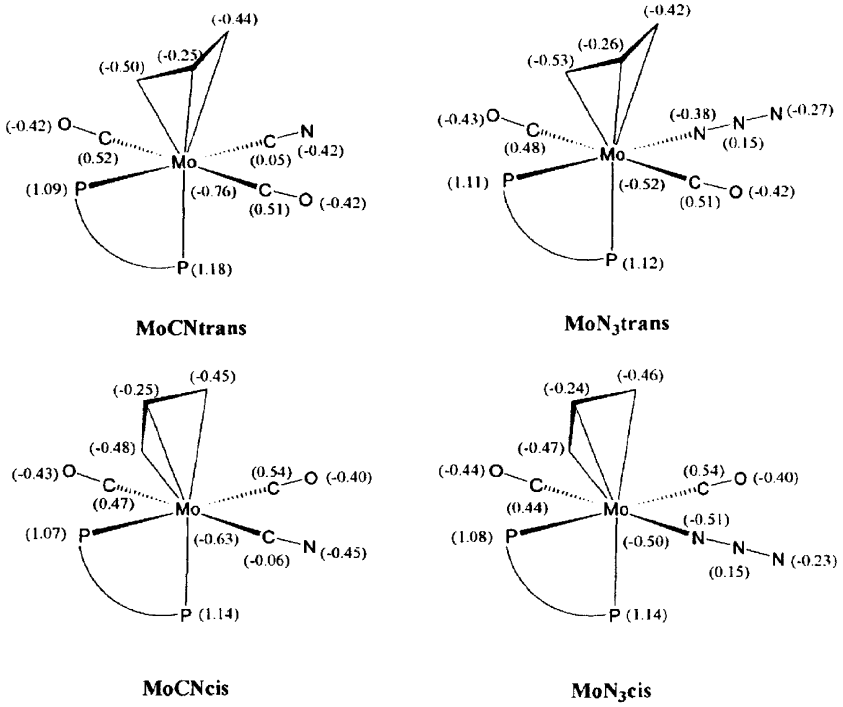

Figure 5. Net natural population analysis charges for **2** and **3**.

etries and energies are given in Figure 4 and Table 2, and the results of the net natural population analysis charges are summarized in Figure 5. The NPA charge[18] on the metal atom of **3** is −0.63 in the *cis* isomer and −0.76 in the *trans* one. The NPA charges on all the ligands are similar in both isomers except for CN^-, which presents a net charge of −0.51 and −0.37 in the *cis* and *trans* structures, respectively.

An analysis of the Kohn−Sham MOs of [Mo(CN)(η^3-C_3H_5)(CO)$_2$(dmpm)] (**3**) in terms of those of the metal atom and the ligands[19] shows that the most important fragment electronic configurations describing the *trans* structure imply electron transfers from the HOMOs of $C_3H_5^-$ and CN^- to the LUMO of Mo^{2+}. In contrast, in the *cis* isomer the relative weight of these electronic configurations considerably diminish, the electron transfers from the HOMOs of the CO ligands to the LUMO of Mo^{2+} becoming dominant, particularly those configurations corresponding to back-donation from the metal to the CO's.

The above-mentioned differences in energy and electronic structure between the *cis* and *trans* isomers of [Mo(CN)(η^3-C_3H_5)(CO)$_2$(dmpm)] can be easily rationalized taking into account the main interactions between CN and the metal atom. As displayed by the diagram in Figure 3, our analysis reveals that, in the *trans* isomer, the HOMOs of CN^- and $C_3H_5^-$ interact mainly with the d_{yz} LUMO of the metal, whereas in the *cis* isomer the HOMO of CN^- and the HOMO of one of the CO ligands present the most important interaction with the $d_{x^2-y^2}$ LUMO of Mo^{2+}. From the diagram it is clear that this different interaction pattern can explain the fact that CN^- behaves as a better electron donor in the *trans* structure and appears to determine the preferential stabilization of that isomer.

Therefore, our theoretical analysis establishes the strong σ-donor character of the cyano ligand as responsible for the encountered difference between the structures of **2** and **3**.[20]

Experimental Section

All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled from Na (hexane), NaOMe (MeOH), and CaH_2 (CH_2Cl_2). CD_2Cl_2 was dried over molecular sieves (4 Å) and stored over Na_2CO_3 in Young tubes in the dark. Elemental analyses were obtained using a Perkin-Elmer 240-B microanalyzer. The IR and NMR spectra were recorded on Perkin-Elmer FT 1720-X (over the

(18) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988.

(19) This analysis was performed by using the ANACAL program: López, R.; Menéndez, M. I.; Suárez, D.; Sordo, T. L.; Sordo, J. A. *Comput. Phys. Commun.* **1993**, *76*, 235−249.

(20) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283.

range 2200−1600 cm^{-1}) and Bruker AC-200 (or AC-300) spectrometers, respectively, using TMS as internal reference.

Synthesis of 1. Under N_2, dmpm (56 μL, 0.35 mmol) was added to a solution of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$[13] (0.110 g, 0.35 mmol) in CH_2Cl_2 (10 mL). After 5 min stirring the volume was reduced in vacuo to 5 mL and hexane (20 mL) was layered, giving (2 days at −20 °C) red crystals of **1**. Yield: 0.120 g, 93%. Anal. Calcd for $C_{10}H_{19}ClMoO_2P_2$: C, 32.94; H, 5.25. Found: C, 33.21; H, 4.97. IR (CH_2Cl_2): 1944(s), 1845(s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −24.38. ^1H NMR (CD_2Cl_2): δ 4.75(m, 1H, H_c); 3.69(m, 2H, H_{syn}); 3.24(m, 2H, CH_2 dmpm); 2.31(d, ^3J(H,H) = 11.7, 2H, H_{anti}); 1.73(t, ^2J(P,H) = 4.8, 6H, CH_3 dmpm); 1.65(t, ^2J(P,H) = 5.2, 6H, CH_3 dmpm). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 226.68(t, ^2J(P,C) = 7.6, CO); 98.68(s, C_2 allyl); 62.36(s, C_1 and C_3 allyl); 40.65(t, ^1J(P,C) = 23.2, CH_2 dmpm); 17.34(t, ^1J(P,C) = 13.6, CH_3 dmpm); 13.40(t, ^1J(P,C) = 12.8, CH_3 dmpm).

Synthesis of 2. Sodium azide (0.017 g, 0.27 mmol) was added to a solution of **1** (0.100 g, 0.27 mmol) in 15 mL of a mixture of CH_2Cl_2/MeOH (5:1, v/v). Stirring (90 min), solvent evaporation in vacuo, extraction of the residue (CH_2Cl_2, 10 mL), filtration (Celite), in vacuo concentration (to 5 mL), and layering with hexane (20 mL) afforded, after 2 days at −20 °C, orange crystals. Yield: 0.01 g, 68.7%. Anal. Calcd for $C_{10}H_{19}MoN_3O_2P_2$: C, 32.36; H, 5.16; N, 11.32. Found: C, 32.56; H, 5.34; N, 11.12. IR (CH_2Cl_2): 2072(s), 1936(s), and 1851(s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.38, s. ^1H NMR (CD_2Cl_2): δ 4.82(m, 1H, H_c); 3.70(m, 2H, H_{syn}); 3.28(at, ^2J(H,P) = 10, 2H, CH_2 dmpm); 2.19(d, ^3J(H,H) = 12, 2H, H_{anti}); 1.71(m, 12H, CH_3 dmpm). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 226.51(at, ^2J(P,C) = 8, CO); 62.30(s, C_1 allyl); 57.86(s, C_2 allyl); 40.93(at, J(P,C) = 24, CH_2 dmpm); 17.56(at, J(P,C) = 15, CH_3 dmpm); 16.43(d, J(P,C) = 23, CH_3 dmpm); 14.62(at, J(P,C) = 11, CH_3 dmpm).

Synthesis of 3. Sodium cyanide (0.016 g, 0.32 mmol) was added to a solution of **1** (0.100 g, 0.32 mmol) in 15 mL of a mixture of CH_2Cl_2/MeOH (5:1, v/v). After 6 h stirring, workup as for **2** gave **3** as a pale yellow powder. Yellow crystals of **3** were obtained by slow diffusion of hexane into a concentrated solution of **3** in CH_2Cl_2 at −20 °C. Yield: 0.078 g, 68.4%. Anal. Calcd for $C_{11}H_{19}MoNO_2P_2$: C, 37.20; H, 5.39; N, 3.94. Found: C, 37.47; H, 5.12; N, 3.72. IR (CH_2Cl_2): 2096(w), 1867(vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −11.4, −21.4 (ABq, ^2J(P,P) = 85.4). ^1H NMR (CD_2Cl_2): δ 5.21(m, 1H, H_c); 3.20(m, 2H, CH_2 dmpm); 3.08(dd, ^3J(P,H) = 7.0, ^2J(H,H) = 3.2, 1H, H_{syn}); 2.77(d, ^3J(H,H) = 12.2, 1H, H_{anti}); 2.21(m, 2H, H_{anti}, H_{syn}); 1.96(d, ^2J(P,H) = 9.8, 3H, CH_3 dmpm); 1.73(t, ^2J(P,H) = 9.9, 6H, CH_3 dmpm); 1.59(d, ^2J(P,H) = 9.1, 3H, CH_3 dmpm). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 211.53(t, ^2J(P,C) = 10.1, CO); 209.33(t, ^2J(P,C) = 8.3, CO); 145.81(d, ^2J(P,C) = 17.1, CN); 98.67(s, C_2 allyl); 53.96(s, C_1 allyl); 45.47(d, ^2J(P,C) = 9.2, C_3 allyl); 40.88(t, ^1J(P,C) = 24, CH_2 dmpm); 20.35(t, ^1J(P,C) = 3.2, CH_3 dmpm); 18.50(t, ^1J(P,C) = 6.0, CH_3 dmpm).

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología (grants BQU2000-0220 and BQU2000-0219) and Principado de Asturias (grants PR-01-GE-7 and PR-01-GE-4) for support of this work.

Supporting Information Available: Tables giving positional and thermal parameters, bond distances and bond angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020919M