

**Table 5. The yield of  $\alpha$ -(2,2-Dinitro-1-phenylethyl)-L-cysteine Derivatives with the Various pH**

pH	Yield of adducts(12a-e), wt., %				
	12a	12b	12c	12d	12e
3.0-3.7	32.5	58.2	72.3	56.3	28.2
4.3-4.5	52.8	65.8	79.2	73.0	36.6
5.8-6.8	72.4	90.8	85.0	90.2	48.6
7.2-7.9	72.4	95.7	85.0	93.5	43.6
8.2-8.9	29.8	78.2	69.8	67.5	8.6
9.4-9.5	small	16.4	43.2	32.8	nothing
9.7-9.8	small	nothing	22.5	12.4	nothing

spectra in dioxane (Table 2) showed marked decrease in absorptions at  $\lambda_{max}$  of corresponding  $\beta$ ,  $\beta$ -dinitrostyrene derivatives, indicating again the absence of carbon-carbon double bond in the adducts. The NMR spectra (Table 3) are in good agreement with the proposed structure (Table 1).

The yields of the products the dependence between  $\beta$ ,  $\beta$ -dinitrostyrene and L-cysteine upon pH were experimented (Table 5). The lower yields observed at lower pH may be ascribed to the decreased concentration of reactive thiolate anion. At higher pH, the competing hydrolysis of  $\beta$ ,  $\beta$ -dinitrostyrene may be predominant, thus decrease the yields.

In spite of many applications of nucleophilic addition reaction, the number of qualitative observations suggest a quite plausible mechanism, it has been the subject of only a few kinetic studies. Thus, attempts have to be made to reveal the exact reaction mechanism<sup>7</sup> of the L-cysteine addition to  $\beta$ ,  $\beta$ -dinitrostyrene in future.

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## The Terminal-Phosphinidene Complexes. Bonding, Geometrical Optimization, and Electronic Considerations

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The molecular interaction and geometrical optimization of  $\text{Cr}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_3$  units have been studied for phosphinidene complex by means of extended Hückel calculations. The results were compared with those of *ab initio* calculations and found to be in qualitative agreement. Geometrical optimization of  $\text{HPCr}(\text{CO})_5$  (1) and  $\text{HPNi}(\text{CO})_3$  (2) gave the values  $R = 2.36 \text{ \AA}$ ,  $\theta = 111.5^\circ$ , and  $\phi = 45^\circ$  for 1, and  $R = 2.37 \text{ \AA}$ ,  $\theta = 120^\circ$ , and  $\phi = 58^\circ$  for 2. It is found that the low rotational barriers for 1(0.46 kcal mol<sup>-1</sup>) and 2(0.12 kcal mol<sup>-1</sup>) would be accompanied by the free rotation, in spite of the fact that both 1 and 2 adopt staggered conformations.

## Introduction

Metal carbene complexes of the type  $\text{R}_2\text{CML}_n$  are of considerable importance as intermediates of many organometallic reactions.<sup>1</sup> Terminal-phosphinidene complexes of the type  $\text{RPML}_n$  which are closely related to metal carbene complexes are of interest as one of the special bonding modes in organometallic chemistry. Recently, such com-

plexes of the transition metals, Cr, Mo,  $\text{W}^2$ , and  $\text{Fe}^3$ , have been reported and known as short-lived species. So far, no crystal structures have yet been reported. As we are interested in the nature of the  $\text{M}=\text{P}$  bond, and the origin of the reactivity of the phosphinidene complexes, we have chosen the hypothetical terminalphosphinidene complexes  $\text{HPCr}(\text{CO})_5$  (1) and  $\text{HPNi}(\text{CO})_3$  (2).

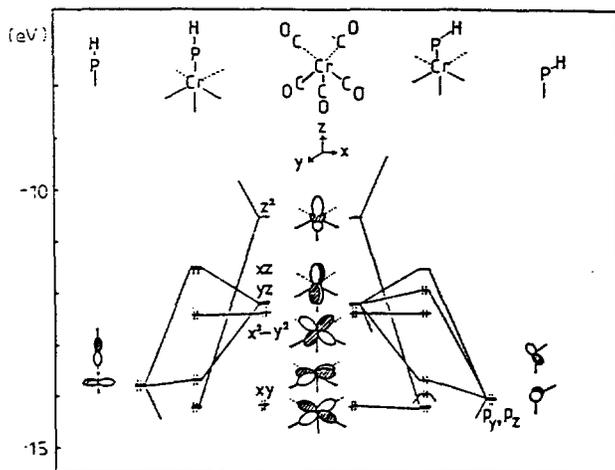


Figure 1. An orbital interaction diagram for  $\text{HPCr}(\text{CO})_5$ .

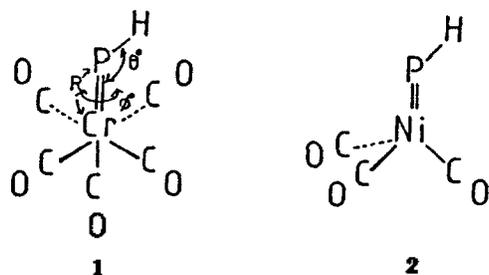


Figure 2. An idealized Walsh diagram for  $\text{HPCr}(\text{CO})_5$ .

Recently, Cowley and coworkers<sup>4</sup> have undertaken an *ab initio* MO calculations of the complexes (1) and (2). They examined the geometrical parameters and discussed the electronic structure of two complexes.

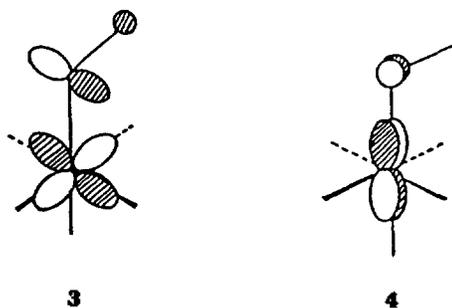
Here, we report the results of extended Hückel calculations of the complexes (1) and (2). We compare the results of extended Hückel calculations with those of *ab initio* MO calculations.

**Phosphinidene- $\text{Cr}(\text{CO})_5$  complex.** In the complex  $(\text{CO})_5\text{CrPH}$ , the ligand  $\text{PH}^{-2}$  will be considered to act as four electron donor in terms of the lower filled energy levels of the ligand than those of metal. Therefore, the  $\text{Cr}^{+2}$  atom has a  $d^4$  configuration. The complex  $(\text{CO})_5\text{CrPH}$  is of the 18 valence electron type, which is at least stable by means of the electron count.

Figure 1 shows an interaction diagram for a phosphinidene and a  $\text{Cr}(\text{CO})_5$  fragments. At the right of the Figure 1 are symmetry adapted linear combinations of the lone pair hybrids on the phosphorus atom,  $\sigma$  and  $\pi$ , with the d orbitals of chromium. In the center of this Figure are the five metal-centered orbitals of a  $\text{Cr}(\text{CO})_5$  fragment. It is most clearly related to an octahedral complex.<sup>5</sup> There is a lower set of three levels,  $e+g_2$ , descended from the octahedral  $t_{2g}$  set. At low energy are two filled  $b_2$  and  $e$ -like orbitals,  $xy$ , and  $xz$ . At higher energy are an empty  $yz$  character and an empty level primarily of  $z^2$  character. The  $z^2$  character is hybridized with metal  $s$  and  $z^2$  so that it extends away from the CO ligands, toward the empty coordination site. At middle energy is  $x^2-y^2$ , which together with  $1a_1$  formed the  $e_g$  in  $\text{ML}_6$ . In the molecular interaction,  $x^2-y^2$  is essentially nonbonding and do not give rise to a conformational preference. At low energy  $P_z$  and  $P_y$  of the phosphinidene mix with  $z^2$  and  $yz$  in a bonding fashion to produce a Cr-P  $\sigma$  bond. At higher energy  $P_x$  and  $P_z$  of the ligand mix with  $xz$  and  $yz$  in an antibonding

fashion to produce a Cr-P  $\sigma^*$  and  $\pi^*$  bond, respectively. A critical feature of this qualitative analysis is that the metal-phosphorus  $\sigma^*$ -bond is formed by electron donation from the HOMO of the phosphinidene hybridized with ligand  $s$ ,  $P_x$  and  $P_z$  to the LUMO of  $\text{Cr}(\text{CO})_5$  ( $xz$  orbital) fragment. The molecular interaction of a linear phosphinidene  $\text{Cr}(\text{CO})_5$  complex (on the left side of Figure 1) is different from that of a bent one. The  $xy$  and  $x^2-y^2$  orbitals actually remain nonbonding like a bent phosphinidene  $\text{Cr}(\text{CO})_5$  complex. The  $P_x$  and  $P_y$  orbitals of the ligand overlaps with  $xz$  and  $yz$  to produce a high-lying, filled and empty antibonding molecular orbital, respectively. The HOMO is formed by the mixing of  $xz$  and  $p_x$  for a linear  $\text{HPCr}(\text{CO})_5$  and rises to a high energy, which is destabilized compared with that of a bent one. This is shown from a Walsh diagram in Figure 2.

The destabilization of the molecular orbital along the reaction path (from a bent one to a linear one) comes from the effective interaction between the  $xy$  and  $p_x$  orbitals in an antibonding fashion. The magnitude of this net destabilization is proportional to the overlap between them. An obvious way to decrease the overlap would be to allow the P-Cr distance to increase going from a bent one to a linear one. The resulting bond lengthening is probably accompanied by the loss of bond energy between P-Cr bond. This tells us the reason why a linear phosphinidene configuration is destabilized and changed into a bent one. The HOMO(3) and LUMO(4) of  $\text{HPCr}(\text{CO})_5$  complex are shown below. The HOMO and



LUMO have large AO coefficients at the phosphorus center [0.05 at  $\text{P}(3s)$ , 0.24 at  $\text{P}(3P_x)$ , and 0.21 at  $\text{P}(3P_y)$  for 3, 0.49 at

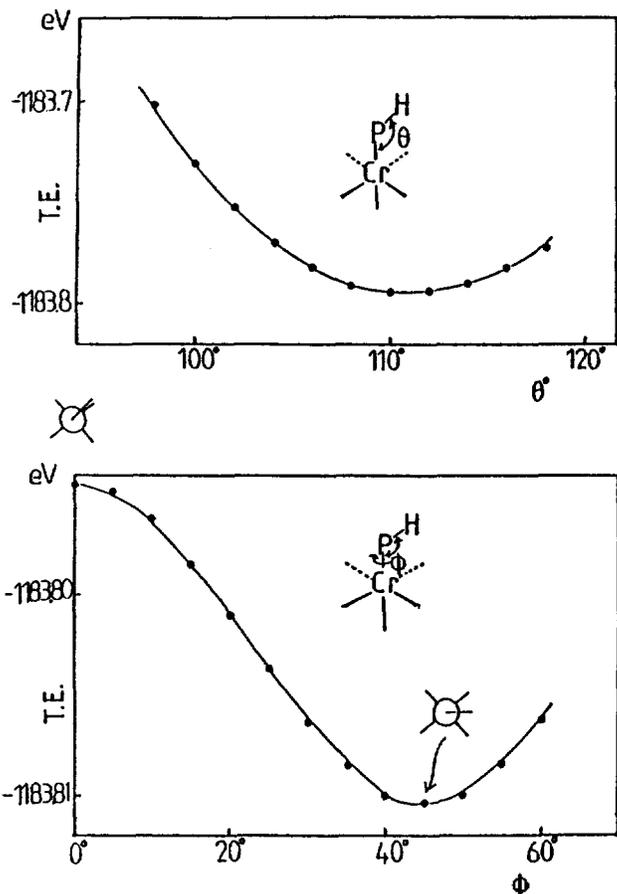


Figure 3. Potential curve for the angle (H-P-Cr) and rotation angle of  $\text{HPCr(CO)}_5$ .

$\text{P}(3p_x)$  and 0.19 at  $\text{P}(3p_y)$  for 4]. The s and p orbital contribution of P to the HOMO and LUMO are relatively large. Consequently, the  $\text{PR}(\text{R}=\text{H})$  ligand is expected to act as a nucleophilic center at phosphorus. In this stage, it is interesting to note three important points for the stability of  $\text{HPCr(CO)}_5$  complex. The first one is the energy gap between the HOMO and LUMO. The second one is the variation of a substituent(R) on the phosphorus. The last one is the discussion of magnetic susceptibility. The energy gap between the HOMO and LUMO is 0.43eV, which is relatively small. The slight energy difference gives rise to the low spin-high spin problem. As indicated above, terminal-phosphinidene complexes have been considered as short-lived species and eluded isolation. It may be attributable to the small energy gap of HOMO and LUMO, resulting in the high spin. The stability of the complex may also depend on the substituent on the phosphorus. When the hydrogen is substituted by an electron-releasing group, the energy difference between the HOMO and LUMO will be increased, making the complex stable in consideration of the spin state. On the other hand, when the hydrogen is substituted by an electron-withdrawing group, the energy gap will be decreased, making the complex unstable. This may lead us to the selection of substituents in order to isolate the terminal-phosphinidene complexes.

Figure 3 shows the total energy of  $\text{HPCr(CO)}_5$  complex with the variation of angle (H-P-Cr,  $\theta$ ) and rotation angle ( $\phi$ ).

The geometry optimization afforded the values  $R=2.35\text{\AA}$

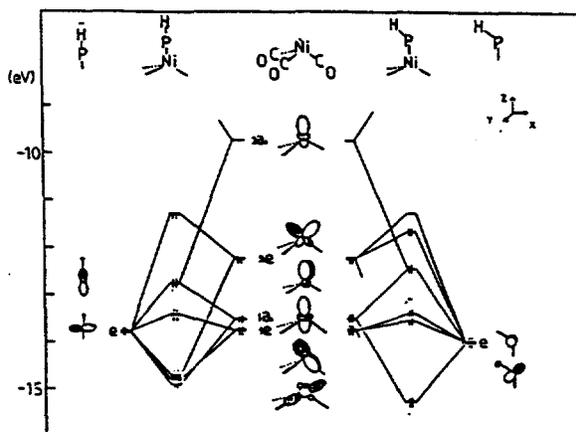


Figure 4. An orbital interaction diagram for  $\text{HPNi(CO)}_3$ .

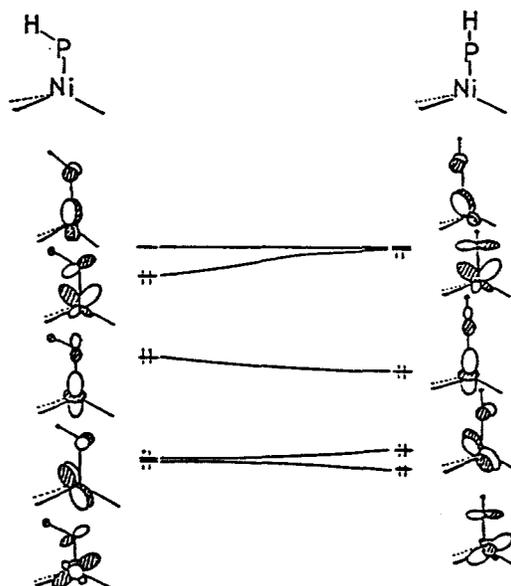


Figure 5. An idealized Walsh diagram for  $\text{HPNi(CO)}_3$ .

$\theta = 111^\circ$ , and  $\phi = 45^\circ$ . The bond length (P-Cr) is close to the sum of the metal-phosphorus covalent radii. Although the minimum energy conformation is staggered from the computed rotational energy ( $0.46 \text{ kcal mol}^{-1}$ ) is very small, resulting in the free rotation. The energy difference is in good agreement with that of *ab initio* calculation ( $0.29 \text{ kcal mol}^{-1}$ ). It is very interesting to note that the total energy for the low spin and high spin state shows the same trends.

**Phosphinidene-Ni(CO)<sub>3</sub> Complex.** Figure 4 shows an interaction diagram for  $\text{HPNi(CO)}_3$  complex. The complex have been divided into  $\text{PH}^{-2}$  anion and  $\text{Ni(CO)}_3$  cation fragments. At the right of Figure 4 is shown the molecular interaction between an bent phosphinidene and  $\text{Ni(CO)}_3$  fragments. The left side of Figure 4 shows a molecular interaction between a linear phosphinidene and  $\text{Ni(CO)}_3$  fragments. For a bent  $\text{HPNi(CO)}_3$ , the e orbital of  $\text{PH}^{-2}$  and  $1a_1$  and  $2a_1$  from  $\text{Ni(CO)}_3^{+2}$  enter into a three orbital pattern. The lowest molecular level consists of the mixing of e(53%) with  $1a_1$  and  $2a_1$  from metal. The middle molecular level is mainly  $1a_1$  and  $2a_1$ . Some e character (27%) mixes into the molecular orbital in an antibonding way. Moreover,  $2a_1$  mixes into it in second order with respect to e. It is the second-order mixing that keeps  $1a_1$  at moderate energy. Three orbital pattern in  $\text{HPNi(CO)}_3$  complex appears in the  $\text{L}_3\text{Fe(CO)}_3^6$  and  $\text{C}_p$

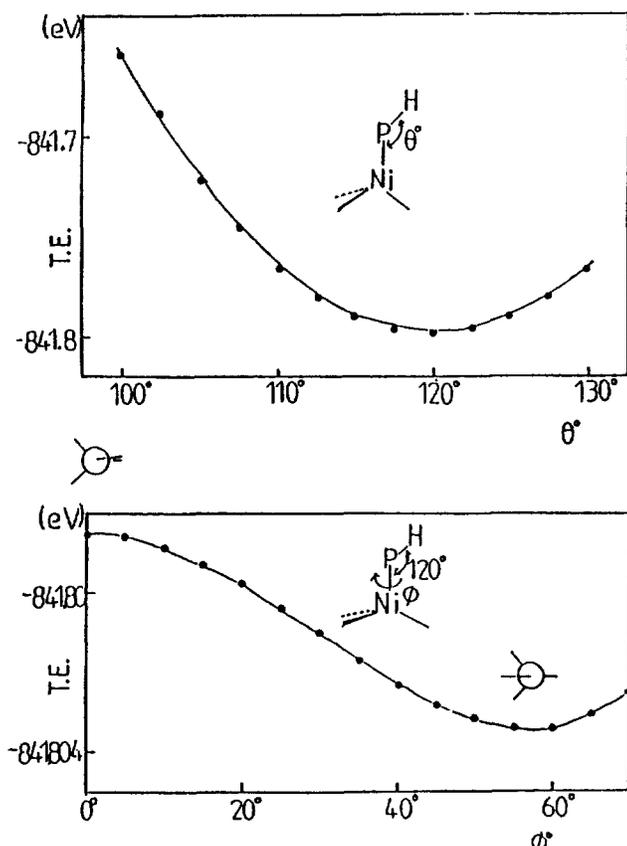


Figure 6. Potential Curve for the low spin of  $\text{HPNi}(\text{CO})_3$ .

$\text{Mn}(\text{CO})_3^7$  complexes in a similar way. At higher energy  $P_x$  and  $P_y$  from the ligand mix with  $2e$  in an antibonding way to produce  $\text{Ni-P} \pi^*$  bond. The highest occupied molecular orbitals are primarily metal  $2e$  antibonding ( $0.11P_x + 0.19x^2y^2 + 0.07z^2 + 0.25xz$ ) to the  $e$  set on the phosphorus center ( $0.055s + 0.14P_x + 0.14P_y$ ). The LUMO has substantial AO coefficients at the phosphorus center [0.32 at  $P(p_x)$ ]. However, the HOMO and LUMO of a bent  $\text{HPNi}(\text{CO})_3$  complex feature small phosphorus AO coefficients compared with those of  $\text{HPCr}(\text{CO})_3$  complex. In view of a relatively low HOMO-LUMO gap (0.4eV) and the substantial contribution of AO coefficients at the phosphorus center, it may be said that the  $\text{HPNi}(\text{CO})_3$  complex is thought as a reactive species toward both nucleophilic and electrophilic reagents. The molecular interaction of a linear phosphinidene  $\text{Ni}(\text{CO})_3$  complex is shown in the left side of Figure 5. In both interactions, three orbital pattern would be preserved. A striking difference between two interaction diagrams arises from the energy level of HOMO. The HOMO for a linear  $\text{HPNi}(\text{CO})_3$  is quite destabilized compared with that of a bent  $\text{HPNi}(\text{CO})_3$  due primarily to the effective overlap of  $p_x$  orbital with  $2e$  from  $\text{Ni}(\text{CO})_3^{-2}$  (see a Walsh diagram in Figure 5). The destabilization of HOMO in  $\text{HPNi}(\text{CO})_3$  complex along the reaction path (from a bent to a linear structure) can be interpreted in a manner almost identical to that of  $\text{HPCr}(\text{CO})_3$  complex. Let us turn to the magnetic susceptibility of  $\text{HPNi}(\text{CO})_3$  complex. The energy difference between the HOMO and LUMO for a bent phosphinidene and a linear phosphinidene  $\text{Ni}(\text{CO})_3$  complexes is 0.4eV and 0.0eV, respectively, which are relatively small. In view of the slight energy difference between two orbitals even for a bent phosphinidene  $\text{Ni}(\text{CO})_3$  complex, the complex would result in the problem of

Table 1. Comparison of the Geometrical Optimization Obtained from *ab initio* Calculations with Those from EH Calculations

	Cr			Ni			
	$r(\text{\AA})$	$\theta^\circ$	$\phi^\circ$		$r(\text{\AA})$	$\theta^\circ$	$\phi^\circ$
EH	2.36	111.5	45	EH	2.37	120	58
<i>ab initio</i>	2.33	110	45	<i>ab initio</i>	2.19	102	30

Table 2. Extended Hückel Calculation Parameters

atom	orbital	$H_{ii}(\text{eV})$	$\xi_{i1}$	$(C_1)^a$	$\xi_{i2}$	$(C_2)^a$	ref
Cr	4S	-8.11	1.7				<i>b</i>
	4P	-5.24	1.7				
	3d	-11.22	4.95	(0.5060)	1.80	(0.6750)	
Ni	4S	-9.17	1.825				<i>c</i>
	4P	-5.15	1.125				
	3d	-13.49	5.75	(5683)	2.00	(0.6292)	
P	3S	-18.6	1.75				<i>b</i>
	3P	-14.0	1.30				
C	2S	-21.4	1.625				<i>b</i>
	2P	-11.4	1.625				
O	2S	-32.3	2.275				<i>b</i>
	2P	-14.8	2.275				
H	1S	-13.6	1.30				<i>d</i>

<sup>a</sup> $C_1$  and  $C_2$  are coefficients in a double- $\xi$  expansion. <sup>b</sup>R.H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976). <sup>c</sup>J.W. Lauber, M. Elian, R.H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976). <sup>d</sup>R. Rein, N. Fukuka, H. Win, G.A. Clarke and F.E. Harris, *J. Chem. Phys.*, **45**, 4773 (1966).

magnetic susceptibility.

Figure 6 shows the total energy of  $\text{HPNi}(\text{CO})_3$  complex with the variation of angle (H-P-Ni,  $\theta$ ) and rotation angle ( $\phi$ ). The geometry optimization afforded the values  $R = 2.37\text{\AA}$ ,  $\theta = 120^\circ$ , and  $\phi = 58^\circ$ . The big difference in angle ( $\phi$ ) between EH and *ab initio* calculations may be attributable to the low rotational barrier. Judged from only steric hindrance, the result obtained from EH calculation may be more reasonable than that from *ab initio* calculation. However, the low rotational barriers would be accompanied by the free rotation. The bond length (P-Ni) is close to the sum of a metal-phosphorus covalent radii. Even though the rotation angle ( $\phi = 58^\circ$ ) adopts a staggered conformation, the extremely small rotational energy ( $0.12 \text{ kcal mol}^{-1}$ ) would lead to the free rotation.

**Summary.** In this paper, we have studied the bonding, and electronic structure of the phosphinidene chromium and nickel complexes, with stress on the bonding of the metal phosphorus double bond. We also obtained the geometrical optimization on the length between metal and phosphorus, angle (M-P-H), and rotation angle ( $\phi$ ). The results (see Table 1) were compared with those of *ab initio* calculations done by Cowley and coworkers. It was found to be in qualitative agreement with those of *ab initio* calculations. It is interesting to note that, although the EHMO is not doing well on the optimization of the length, the calculation of distance between the metal and phosphorus is in good agreement with that of *ab initio* calculations. Through this study, we found that the cheap and simple EHMO gave a reliable value in the geometri-

cal optimization. Since *ab initio* MO calculations give good information on the magnetic susceptibility, it can be said that the combination of EH and *ab initio* MO calculations would give more informations on the analysis of transition metal complexes.

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### Appendix

The M-C and C-O distances for chromium and nickel complexes are based on the  $\text{H}(\text{HO})\text{CCr}(\text{CO})_5^8$  and  $\text{Ni}(\text{CO})_4^9$ , respectively. The P-H distance was assumed to be 1.42 Å in both complexes. All calculations employed M-C-O angles of 180°. The extended Hückel calculations used a modified Wolfsberg-Helmholz formula with the parameters listed in Table 2. Orbital exponents and  $H_{ii}$ 's for Ni and Cr were obtained from previous work.

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## Bonding and Electronic Considerations in the Apex Bridged $\text{M}_2(\text{OR})_6\text{L}_x(\mu\text{-X})$ Complexes ( $\text{M} = \text{Mo}$ ; $\text{R} = -t\text{-Bu}$ , $-i\text{-Pr}$ ; $\text{L} = \text{Py}$ ; $x = 0$ or $2$ ; $\text{X} = \text{CO}$ , $\text{SO}_2$ , $\text{HCCH}$ , $\text{H}$ , and $\text{Cl}$ )

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The molecular interaction of  $\text{Mo}_2(\text{OR})_6(\mu\text{-OR})_2$  unit has been studied for carbonyl and acetylene ligands by means of extended Hückel calculations. We have extended the extended Hückel calculations to unknown apex bridged  $\text{Mo}_2(\text{OR})_6(\mu\text{-X})$  complexes ( $\text{X} = \text{SO}_2$ ,  $\text{H}$ , and  $\text{Cl}$ ) in order to compare the stability of the complexes. In the  $\text{C}_2\text{H}_2$  and  $\text{H}$  apex bridged complexes, one finds a relatively small HOMO-LUMO gap. However, both complexes are stabilized due to Jahn-Teller distortion. The stability of both complexes is comparable to that of  $\text{Mo}_2(\text{OR})_6(\text{CO})$  complex. The comparisons and predictions in the stability of known and unknown complexes are the subject of this study.

### Introduction

The M-M bonded complexes  $\text{M}_2(\text{OR})_6^1$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ;  $\text{R} = \text{Pr}$ ,  $\text{Ne}$ ,  $\text{Bu}$ ) show many striking features.<sup>2</sup> The first thing is that the  $\text{M}_2(\text{OR})_6$  complexes provide a good source of electrons to ligands that are capable of being reduced upon coordination. As an example, carbon monoxide reacts with  $\text{M}_2(\text{OR})_6$  to give the adduct  $\text{M}_2(\text{OR})_6(\mu\text{-CO})^3$ , in which the C-O bond order may be reduced. The second thing is that the  $\text{M}_2(\text{OR})_6$  complexes are coordinatively unsaturated. Therefore, donor ligands rapidly react with the alkoxides  $\text{M}_2(\text{OR})_6$  ( $\text{M} = \text{M}$ ) to give adduct  $\text{M}_2(\text{OR})_6\text{L}_x^4$ , in which one or two alkoxy groups are bridged. For example, acetylene and phosphorus react with the  $\text{Mo}_2(\text{OR})_6$  complexes to give the com-

plexes of the type  $\text{M}_2(\text{OR})_6\text{L}_x$  ( $\text{RCCR}$ )<sup>5</sup> and  $\text{M}(\text{OR})_6\text{L}_x(\text{PP})^6$  ( $\text{R} = \text{Pr}$ ,  $\text{CH}_2-t\text{-Bu}$ ,  $\text{Bu}$ ;  $\text{L} = \text{py}$ ;  $\text{R} = \text{H}$  and  $\text{Me}$ ), respectively. The geometry of the  $\text{M}_2(\text{OR})_6(\mu\text{-X})$  complexes is an square based pyramidal for molybdenum atom through the agency of alkoxy bridges, in which an incoming ligand may be sited at an apical position. The metal-metal complexes with alkoxy bridges, in which access to two metals is controlled by the alkoxy ligands, offer the possibility of activation of substrates.

Recently, Chisholm and coworkers<sup>7</sup> reported the bonding in monocarbonyl adducts of dimolybdenum and ditungsten hexaalkoxides with the aid of nonparameterized Fenske-Hall calculations. Since we are interested in the electronic structure and stability of various apical ligands ranging from sin-