with the complete incorporation of ^{18}O into the product when the monooxygen atom donor $PhI^{18}O$ is used. The high-spin d^5s formulation for the valence electrons of the iron centers is supported by the electrochemical and magnetic measurements. The product from the combination of $(Cl_8TPP)Fe^+$ and ^-OH, $(Cl_8TPP)Fe\text{-}OH$, has a magnetic moment of 5.5 μ_B, which is consistent with d^5sp^2 valence-electron hybridization.[24] The assignment of the Raman band at 882 cm^{-1} to a dioxygen bridge (FeOOFe) is supported by the ^{18}O-labeling experiment and the similarity of the band to that for free HOOH (877 cm^{-1}).[22] Likewise, the electrochemical oxidation at +1.8 V vs SCE is closely similar to that for HOOH in MeCN ($\mathbf{1} \xrightarrow{-2e^-} 2L_4Fe^{3+} + O_2 + 2HOH$). The potential shift of +0.7 V (from the +1.1 V value for the L_4Fe^{2+}/L_4Fe^{3+} couple) is a measure of the covalent-bond formation energy for $[L_4Fe\text{–}OOFeL_4]^{4+}$ $[(-\Delta G)_{BF} = 0.7 \times 23.1 = 16$ kcal].[25] Because $(-\Delta G)_{BF}$ for the H–OOH bond is about 80 kcal, the $[L_4FeO\text{–}OFeL_4]^{4+}$ bond energy should be substantially greater than that for the HO–OH bond ($\Delta H_{BDE} = 51$ kcal).[26] Addition of excess ^-OH to **1** induces its rapid decomposition to $Fe(OH)_3$ and HOOH, which is consistent with these estimated bond energies.

Additional support for the formulation of **1** is provided by its stoichiometric synthesis from the combination of 2 mol of $[Fe^{III}(Ph_3PO)_4](ClO_4)_3$ with 1 mol of HOOH plus 2 mol of ^-OH (eq 2).

$$[Fe^{III}(Ph_3PO)_4]^{3+} + HOOH + 2\,^-OH \rightarrow \mathbf{1} \qquad (2)$$

The formation of **1** via the processes outlined in Scheme I appears to be unique and represents a novel route to the formation of a μ-dioxygen bridge by a $L_4Fe(O)/L_4Fe(O)$ coupling reaction. In contrast, formation of a μ-oxo dimer by addition of $Fe^{II}(OPPh_3)_4{}^{2+}$ to **2** does not occur and appears to be precluded by the steric effects of the triphenylphosphine oxide ligands.

Reactivity of 1. The binuclear μ-dioxygen complex (**1**) reacts with ^-OH, pyridine, and other Lewis bases with a stoichiometry of two base molecules per **1**. The reactivity of **1** with HX (X = Cl, Br, I) and R_4NX (X = Br, I) is summarized in Scheme I. Chloride ion in the absence of protons is different from the other halides because it is an inadequate reductant. Instead, addition of Cl^- appears to occur via a sequential process such that a monochloro derivative and a dichloro derivative are formed (see Figure 2).

The dioxygenation by **1** of PhC≡CPh is particularly compelling evidence in support of the μ-dioxygen formulation for **1**.

$$\mathbf{1} + PhC{\equiv}CPh \rightarrow PhC(O)C(O)Ph + 2L_4Fe^{2+} \qquad (3)$$

Although Ph_3PO is not a biological ligand, the halochemistry of Scheme I may be relevant to the myeloperoxidase (MPO, a heme protein) activation of Cl^- and HOOH.[27]

$$Cl^- + HOOH \xrightarrow{MPO} {}^-OCl + H_2O \qquad (4)$$

Some of these intermediates may be similar to the intermediate in the $Fe^{III}Cl_3/H_2O_2/RH$ system in MeCN,[17] which is highly efficient for the epoxidation of olefins and for the chlorination of PhCH(O) to PhC(O)Cl and of cyclohexane to cyclohexyl chloride.

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Theoretical Study of the Cis–Trans Isomerism in Disubstituted d^6 Metal Carbonyls

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The relative stability of the cis and trans isomers of the disubstituted d^6 metal carbonyls $M(CO)_4L_2$ (M = Cr, Mo and L = NH_3, PH_3, C_2H_4) and $M(CO)_4LL'$ (M = Mo, L = C_2H_4, L' = CH_2) has been studied theoretically through ab initio SCF calculations. Correlation effects were studied for $Cr(CO)_4L_2$ with L = NH_3, PH_3, C_2H_4 through CAS SCF (complete active space SCF) calculations. The results may be summarized as follows: (i) for $M(CO)_4L_2$, with L = NH_3, PH_3, the cis isomer is more stable than the trans one; (ii) for $M(CO)_4L_2$ with L = C_2H_4 or $M(CO)_4LL'$ with L = C_2H_4 and L' = CH_2, the trans isomer is more stable than the cis one; (iii) going from Cr to Mo increases the stability of the cis isomer for L = NH_3, PH_3 but decreases it for L = C_2H_4. These theoretical results are in excellent agreement with the bulk of structural data. The results for L = NH_3, PH_3 are understood easily in terms of competition for π back-bonding, but no simple rationale emerges for the greater stability of the trans structure in the case of ethylene or carbene ligands.

Introduction

Much theoretical work has been devoted to the study of the conformation of organometallics.[1] Comparatively, few theoretical studies deal with the relative stability of geometrical isomers. Noell and Hay studied the structures and relative energies of the cis and trans isomers of $Pt(PH_3)_2XY$ (with X, Y = H, Cl) and of $Pt(CH_3)_2H_2$.[2,3] The $Pt(PH_3)_2H_2$ system was also investigated by Morokuma et al.[4] Dedieu has calculated the relative stabilities of the most probable stereoisomers for the rhodium complexes $RhClL_2$, H_2RhClL_3, H_2RhClL_2, $H_2RhClL_2(C_2H_4)$, and $H_2RhClL_2(C_2H_5)$.[5] He also investigated the cis–trans conformational isomerism of $H_2Fe(CO)_4$.[6]

For the disubstituted d^6 metal carbonyls $M(CO)_4L_2$, two stereoisomers are possible, namely the cis **1** and the trans **2**. For organometallics with a coordination number of 6, the octahedron is usually rather rigid[7] and structures such as **1** and **2** do not interconvert easily (although polytopal rearrangement has been reported in a number of cases[8-14]). For these systems, the question

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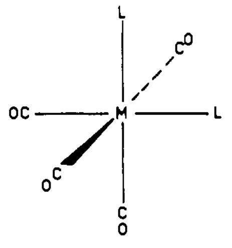

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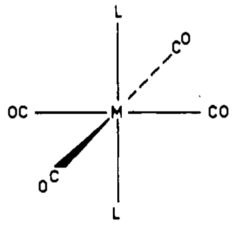

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of knowing which is the most stable isomer is raised on many occasions:

(i) The photosubstitution of monosubstituted d^6 metal carbonyls $M(CO)_5L$

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO$$

is highly stereospecific, yielding in most cases the cis isomer.[15] Does this stereospecificity reflect kinetic or thermodynamic factors?

(ii) In these photosubstitution reactions, the only systematic exception to the cis stereospecificity seems to occur when L and L′ are olefinic ligands, leading in these cases to the trans derivative.[17-20] This has been ascribed to a thermodynamic instability of the cis derivative relative to the trans one.[16] More recently the observation has been reported of both the *cis*-$Cr(CO)_4(C_2H_4)_2$ and the *trans*-$M(CO)_4(C_2H_4)_2$ (M = Cr, Mo, W) compounds[21-23] (with the greater stability of the trans derivative confirmed for $Cr(CO)_4(C_2H_4)_2$).

(iii) Photolysis of $W(CO)_5CPh_2$ at 25 °C in the presence of a linear alkene results in metathetical exchange, probably through the formation of an intermediate cis alkylidene/alkene complex,[24] while its photochemical reaction with cyclooctene at −60 °C gives a trans carbene (olefin) complex.[25] We have previously interpreted these results on the basis of the trans carbene (olefin) complex being thermodynamically more stable than the cis isomer.[16] This has been experimentally confirmed by the synthesis of alkene–carbene complexes in which the two functions are trans (although the kinetic product is probably the cis complex).[26]

(iv) The most studied of these disubstituted derivatives are certainly the phosphine-substituted complexes. Results regarding the relative stability of the cis and trans derivatives may be summarized as follows: There is a tendency to isomerize to the trans structure when the steric bulk of the PR_3 ligands increases.[27] For instance, while $Cr(CO)_4(PH_3)_2$ exists in the cis form,[28] the species $Cr(CO)_4(PMe_3)_2$ favors the trans stereochemistry and $Cr(CO)_4(PEt_3)_2$ exists predominantly in the trans isomeric form.[29] For the compounds $Mo(CO)_4(PR_3)_2$, the cis stereochemistry is slightly favored for R = Me but not for R = Et, *n*-Bu, Ph.[9,30,31] The trans isomer is thermodynamically more stable by about 1 kcal/mol for L = P-*n*-Bu_3, PEt_3 and by perhaps 2-3 kcal/mol for L = PPh_3.[31] Going from chromium to molybdenum displaces the equilibrium toward the cis isomer.[12,32]

Table I. Relative SCF and CAS SCF Energy (in kcal/mol) of the Cis and Trans Isomers of the Systems $M(CO)_4L_2$ and $M(CO)_4LL'$

	ΔE(cis–trans)	
	SCF	CAS SCF
$Cr(CO)_4(NH_3)_2$	2.1[a] 1.2[b]	−13.2
$Cr(CO)_4(PH_3)_2$	−0.4	−2.1
$Mo(CO)_4(NH_3)_2$	−11.5	
$Mo(CO)_4(PH_3)_2$	−8.9	
$Cr(CO)_4(C_2H_4)_2$	−2.0	6.3
$Mo(CO)_4(C_2H_4)_2$	4.0	
$Mo(CO)_4(C_2H_4)(CH_2)$	8.6	

[a] With the bond lengths of ref 33. [b] With the Cr–C bond lengths set equal to 1.907 Å.

The only previous theoretical study of the cis–trans isomerism in these disubstituted derivatives is the one by Marynick et al.[33] based on PRDDO calculations for $M(CO)_4(NH_3)_2$ with M = Cr^0, Mn^+, Fe^{2+}, Co^{3+}, $Cr(CO)_4(N_2)_2$, and $Cr(CO)_4(PH_3)_2$. The cis conformations of $Cr(CO)_4(NH_3)_2$ and $Cr(CO)_4(N_2)_2$ were favored by 6 and 1.6 kcal/mol, respectively. For $Cr(CO)_4(PH_3)_2$ the isomerization energy was close to zero.

We have reinvestigated this problem by carrying out ab initio SCF and CAS SCF calculations for the systems $M(CO)_4L_2$ (with M = Cr, Mo and L = NH_3, PH_3, C_2H_4) and $M(CO)_4LL'$ (with M = Mo, L = C_2H_4, and L′ = CH_2). Our purpose was to assess the values of the isomerization energies, which may be needed to elucidate certain reaction mechanisms.

Calculations

The calculations were carried out for the two structures, cis and trans, of each system. Although an accurate calculation would require a complete geometry optimization for each structure, we have used somewhat idealized geometries, which are described in the Appendix. The SCF calculations were carried out with the system of programs Asterix,[34] using the following Gaussian basis sets: for molybdenum a (16,11,9) set contracted to [7,5,5],[35] for chromium a (14,9,6) set contracted to [6,4,3],[38] for phosphorus a (11,7) set[40] contracted to [4,3], for the first-row atoms a (9,5) set[40] contracted to [3,2], and for hydrogen a (4) set[40] contracted

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to [2] (namely the contracted basis set is single-ζ for the core orbitals, double-ζ for the valence orbitals and the metal ($n + 1$)p orbitals, triple-ζ for the metal ($n + 1$)s and 3d orbitals, and quadruple-ζ for the metal 4d orbitals). The SCF calculations were performed for the closed-shell configurations, which are reported with the corresponding energy values in the Appendix.

Correlation effects were studied for $Cr(CO)_4(NH_3)_2$, $Cr(CO)_4(PH_3)_2$, and $Cr(CO)_4(C_2H_4)_2$ through CAS SCF (complete active space SCF) calculations.[41] Only the π correlation effects were included, since it is the $d\pi$–$p\pi$ back-bonding that seems to be responsible for the greater stability of one isomer over the other (cf. below). The set of active CAS SCF orbitals includes three strongly occupied orbitals that are mainly of $3d_\pi$ character and three weakly occupied orbitals, mainly of $4d_\pi$ character, used to correlate the first ones. This set of active orbitals is populated by six electrons, and these calculations are referred as CAS SCF 6a6e. The corresponding energy values are given in the Appendix.

Results and Discussion

Our discussion will center on the relative energies of the cis and trans isomers (Table I). We shall discuss first the theoretical results. Next we shall compare them to the experimental data, and finally we shall try to rationalize them.

For $Cr(CO)_4(NH_3)_2$, the trans isomer is marginally more stable than the cis isomer, by about 1–2 kcal/mol, at the SCF level. However, at the CAS SCF level, the cis isomer becomes more stable than the trans one by 13.2 kcal/mol.[42] This is comparable to the situation found for $Fe(CO)_4H_2$, where the inclusion of correlation effects was necessary in order to account for the greater stability of the cis isomer.[6]

For $Cr(CO)_4(PH_3)_2$, the greater stability of the cis isomer increases from 0.4 kcal/mol at the SCF level to 2.1 kcal/mol at the CAS SCF level. Thus, although correlation increases the stability of the cis isomer for both ligands NH_3 and PH_3, this increase is considerably reduced for PH_3 compared to that for NH_3.

For $Mo(CO)_4(NH_3)_2$ and $Mo(CO)_4(PH_3)_2$, the cis isomer is already more stable than the trans one by several kilocalories per mole at the SCF level (respectively 11.5 and 8.9 kcal/mol). From the results obtained for the analogous Cr derivatives, we may infer that this greater stability of the cis derivative will be appreciably increased by correlation effects for the NH_3 ligand but only marginally increased for the PH_3 ligand.

For $Cr(CO)_4(C_2H_4)_2$, the cis isomer is slightly more stable than the trans one at the SCF level (by 2.0 kcal/mol). This order of stability is reversed at the CAS SCF level, with the trans isomer now more stable than the cis one by 6.3 kcal/mol.

For $Mo(CO)_4(C_2H_4)_2$ and $Mo(CO)_4(C_2H_4)(CH_2)$, the trans isomer is more stable than the cis one at the SCF level (by 4.0 and 8.6 kcal/mol). For $Mo(CO)_4(C_2H_4)_2$ we expect that this greater stability of the trans isomer will be increased by the inclusion of correlation effects, in analogy with the results obtained for $Cr(CO)_4(C_2H_4)_2$.

The above results may be summarized in the following way.

(i) For L = NH_3, PH_3, the cis isomer is more stable than the trans one; correlation effects appear to contribute predominantly to this greater stability of the cis isomer for L = NH_3, but their effect is much smaller for L = PH_3.

(ii) For L = C_2H_4, CH_2, the trans isomer is more stable than the cis one and the correlation effects seem to contribute significantly to this greater stability of the trans isomer (at least for $Cr(CO)_4(C_2H_4)_2$).

(iii) Judging from the SCF results, going from Cr to Mo increases the stability of the cis isomer for L = NH_3, PH_3 but decreases it for L = C_2H_4.

Before trying to rationalize these results, we shall compare them to the experimental data. The greater stability of the cis isomer for $M(CO)_4L_2$ with M = Cr, Mo and L = NH_3, PH_3 is in agreement with the cis structures reported experimentally.[28,43] That the cis isomer is comparatively more stable for the molybdenum derivatives than for the chromium ones for L = NH_3, PH_3 is in agreement with the experimental trend reported for L = PMe_3, with the trans stereochemistry favored for $Cr(CO)_4(PMe_3)_2$[29] but the cis stereochemistry favored for $Mo(CO)_4(PMe_3)_2$.[30]

The greater stability of the trans structure for $M(CO)_4(C_2H_4)_2$ with M = Cr, Mo is in agreement with the trans structures that have been reported experimentally for Cr, Mo, and W tetracarbonyl bis(olefin) systems.[19,20,23,44] We note that, although both cis and trans structures have been observed experimentally for $Cr(CO)_4(C_2H_4)_2$,[21-23] the trans structure appears to be thermodynamically more stable[21,23] (although kinetic control at the level of the photochemical reaction may result in the production of the cis isomer only,[22] in agreement with the theoretical predictions[16]).

The greater stability of the trans structure for $Mo(CO)_4(C_2H_4)(CH_2)$ is in agreement with the trans structures that have been reported experimentally for alkene–carbene complexes of tungsten.[25,26] We also note that in the work of ref 26, although the cis alkene–carbene complex is probably the kinetic product of the initial photoreaction (in agreement with our theoretical prediction[16]), only the trans product is obtained, as a consequence of the higher stability of this trans isomer.

Ideally, one would like to identify the factors that are responsible for the greater stability of one isomer over the other. We discuss first the case of the complexes with the ligands NH_3 and PH_3. For these small ligands, steric effects may be discarded and the electronic factor responsible for one isomer being preferred is π back-bonding from the metal t_{2g} orbitals to the carbonyls (Burdett has shown that, to first order, σ interactions alone yield equal stability for the two isomers[45]). If L is a σ donor only, π back-bonding will be enhanced for the carbonyl ligands trans to L, compared to carbonyl ligands which are mutually trans. Since the cis isomer reduces the number of mutually trans carbonyls, it should be preferred.[33] This rationalizes the greater stability of the cis structure for $M(CO)_4L_2$ (L = NH_3, PH_3). The same argument also accounts for the increased stability of the cis structure when the correlation effects are included, since π back-donation is enhanced through these correlation effects.[6,46-50] It also accounts for the increased stabilization of the cis isomer when going from chromium to molybdenum, since the latter is expected to be a better π-donor than the former.[51] Finally the reduction in the cis–trans isomerization energy as one goes from $M(CO)_4(NH_3)_2$ to $M(CO)_4(PH_3)_2$ has been ascribed by Marynick to the fact that PH_3 is not a pure σ donor but can also act as a π acceptor, in contrast to the case for NH_3.[33,53]

In contrast to the complexes with NH_3 and PH_3 ligands, which favor the cis structure, the bis(ethylene) and the ethylene–carbene complexes prefer the trans structure. A qualitative explanation of the greater stability of the trans bis(alkene) complexes has been advanced in terms of competition for π back-bonding,[25,54] namely that a trans CO group will weaken the M–alkene bond (since there will always be competition for the d_π electrons between C_2H_4 and a CO group trans to it, while there will be no competition between two trans C_2H_4 groups, provided that they are mutually perpendicular[55]), with the cis compound being less stable than the trans

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since it has two sets of CO and C_2H_4 ligands mutually trans while the trans compound has none. However, this argument does not consider the totality of the carbonyl ligands in the competition for π back-bonding, and a more thorough analysis should consider the whole set of π interactions. In the trans compound, one ethylene and two carbonyl ligands compete for the d_{xz} electrons, a similar set compete for the d_{yz} electrons, and four carbonyl ligands compete for the d_{xy} electrons. In the cis compound, one ethylene and three carbonyl ligands compete for the d_{xz} electrons, a similar set compete for the d_{yz} electrons, and two carbonyl ligands compete for the d_{xy} electrons. In fact there seems to be no simple rationale to favor one isomer over the other. Besides, the greater stability of the trans structure does not seem to result from the sole steric repulsion between the ethylene ligands, since extended Hückel calculations[56] for $Cr(CO)_6$ with two single-face π-acceptor carbonyl ligands (mimicking the π-acceptor character of the ethylene ligands), either cis or trans, indicate a slightly greater stability (of about 2 kcal/mol) of the trans derivative. This conclusion is reinforced by the greater stability of the trans structure for the ethylene–carbene complex, since the steric repulsion should be much reduced in this system.

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Appendix

The geometries used in the calculations were obtained by assuming the following bond lengths and bond angles.

The ligand–metal–ligand angles were set equal to 90° (regular octahedron).

For $Cr(CO)_4L_2$ (L = NH_3, PH_3), we have used the bond lengths of ref 33 (either optimized or assumed). For *cis*-$Cr(CO)_4(NH_3)_2$, we have carried out two calculations, which differ only in the Cr–C bond lengths. In the first one, we used the Cr–C bond lengths of ref 33 (1.881 Å for C trans to NH_3 and 1.900 for C trans to CO); in the second one, we have used a Cr–C bond length of 1.907 Å corresponding to the value optimized for the trans compound in ref 33.

For *cis*-$Mo(CO)_4(NH_3)_2$, Mo–N = 2.269 Å, Mo–C = 2.056 Å (for CO cis to NH_3), and Mo–C = 2.035 Å (for CO trans to NH_3).[57]

For *trans*-$Mo(CO)_4(NH_3)_2$, Mo–N = 2.271 Å and Mo–C = 2.075 Å.[57]

For *cis*-$Mo(CO)_4(PH_3)_2$, Mo–P = 2.447 Å, Mo–C = 2.043 Å (for CO cis to PH_3), and Mo–C = 2.034 Å (for CO trans to PH_3).[57]

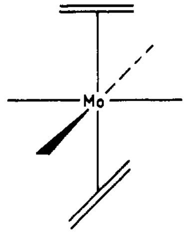
For *trans*-$Mo(CO)_4(PH_3)_2$, Mo–P = 2.405 Å and Mo–C = 2.159 Å.[57]

For $Mo(CO)_4L_2$, the CO bond length and the geometrical parameters for the ligands NH_3 and PH_3 were identical with those used for $Cr(CO)_4L_2$.

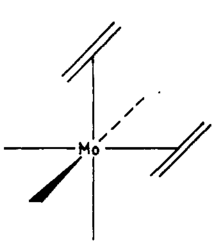
For $Cr(CO)_4(C_2H_4)_2$, $Cr–C_{CO}$ = 1.90 Å, $Cr–C_{C_2H_4}$ = 2.196 Å, C–C = 1.41 Å, C–H = 1.09 Å, and C–O = 1.15 Å. For the trans structure **3**, the two ethylene ligands are mutually staggered and eclipse the carbonyl ligands.[55] For the cis structure **4**, the C–C axes of the two ethylene ligands are parallel.

For $Mo(CO)_4(C_2H_4)_2$, $Mo–C_{CO}$ = 2.00 Å and $Mo–C_{C_2H_4}$ = 2.29 Å, the other parameters being identical with those used for $Cr(CO)_4(C_2H_4)_2$.

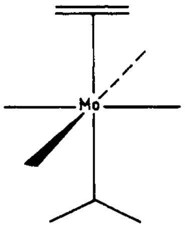
For *trans*-$Mo(CO)_4(C_2H_4)(CH_2)$, $Mo–C_{CO}$ = 2.067 Å, $Mo–C_{C_2H_4}$ = 2.341 Å, $Mo–C_{CH_2}$ = 2.067 Å, C–C = 1.389 Å, $C–H_{C_2H_4}$ = 1.10 Å, and $C–H_{CH_2}$ = 1.07 Å,[59] with the molybdenum atom, the carbene ligand, and the C–C axis of ethylene being in the same plane[25] as shown in **5**.



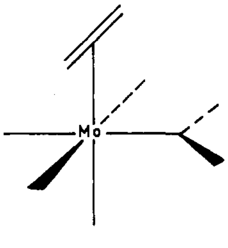
3



4



5



6

For *cis*-$Mo(CO)_4(C_2H_4)(CH_2)$, $Mo–C_{CO}$ = 2.02 Å for the carbonyl ligands trans to each other, $Mo–C_{CO}$ = 1.97 Å for the carbonyl ligands trans to the carbene and ethylene ligands, $Mo–C_{C_2H_4}$ = 2.45 Å, and $Mo–C_{CH_2}$ = 2.127 Å, the other bond lengths being identical with those used for the trans compound.[61] The ligands carbene and ethylene sit in parallel planes, with the axes of the $M—C_{carbene}$ and C═C bonds perpendicular,[65] as shown in **6**.

The molecular point group, the electronic configuration of the SCF wave function, and the SCF and CAS SCF total energies (in au, CAS SCF value in parentheses) were as follows.

$Cr(CO)_4(NH_3)_2$: cis, C_s, $(33a')^2(17a'')^2$, −1603.950 49 (with the bond lengths of ref 33), −1603.952 05 (with the Cr–C bond lengths set equal to 1.907 Å) (−1604.126 54); trans, C_{2v}, $(25a_1)^2(3a_2)^2(10b_1)^2(12b_2)^2$, −1603.953 95 (−1604.105 45).

$Cr(CO)_4(PH_3)_2$: cis, C_s, $(37a')^2(21a'')^2$, −2175.699 12 (−2175.867 97); trans, C_{2v}, $(28a_1)^2(4a_2)^2(13b_1)^2(13b_2)^2$, −2175.698 47 (−2175.864 58).

$Mo(CO)_4(NH_3)_2$: cis, C_s, $(39a')^2(20a'')^2$, −4530.280 88; trans, C_{2v}, $(29a_1)^2(4a_2)^2(12b_1)^2(14b_2)^2$, −4530.262 64.

$Mo(CO)_4(PH_3)_2$: cis, C_s, $(43a')^2(24a'')^2$, −5102.034 30; trans C_{2v}, $(32a_1)^2(5a_2)^2(15b_1)^2(15b_2)^2$, −5102.020 10.

$Cr(CO)_4(C_2H_4)_2$: cis, C_{2v}, $(23a_1)^2(6a_2)^2(14b_1)^2(13b_2)^2$, −1647.530 25 (−1647.687 22); trans, D_{2d}, $(13a_1)^2(2a_2)^2(3b_1)^2(12b_2)^2(13e)^4$, −1647.527 12 (−1647.697 23).

$Mo(CO)_4(C_2H_4)_2$: cis, C_{2v}, $(27a_1)^2(7a_2)^2(16b_1)^2(15b_2)^2$, −4573.829 30; trans, D_{2d}, $(15a_1)^2(2a_2)^2(4b_1)^2(14b_2)^2(15e)^4$, −4573.835 67.

$Mo(CO)_4(C_2H_4)(CH_2)$: cis, C_s, $(41a')^2(20a'')^2$, −4534.810 37; trans, C_{2v}, $(28a_1)^2(5a_2)^2(13b_1)^2(15b_2)^2$, −4534.824 00.

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(57) These values were assumed on the basis of the bond lengths optimized in ref 33 for $Cr(CO)_4(NH_3)_2$ and $Cr(CO)_4(PH_3)_2$ and reported in the literature for $Cr(CO)_5P(C_6H_5)_3$[58] and $Mo(CO)_5P(C_6H_5)_3$.[58]

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(59) On the basis of the structural data for $Ph_2C═W(CO)_4(\eta^2$-*trans*-cyclooctene).[25] Experimental evidence suggests that the bond distances for the second- and third-row metals will be similar.[60]

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(61) On the basis of the structural data reported for cis carbene–alkene complexes.[62,63] The $Mo–C_{CH_2}$ bond length in the cis isomer was assumed to be 0.06 Å longer than in the trans isomer.[64]

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