Do Spin State Changes Matter in Organometallic Chemistry? A Computational Study

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Abstract: Spin changes occur often in organometallic chemistry, and their effect on kinetics is not well understood. We report computations on the singlet and triplet potential energy surfaces of several processes of this type and show that the topology of the individual surfaces, as well as of the crossing regions between them, can be used to rationalize the observed reactivity in all cases. In particular, the slow addition of dihydrogen to W[N(CH$_2$CH$_2$NSiMe$_3$)$_3$]H (Schrock, R. R.; Shih, K. Y.; Dobbs, D. A.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 6609) is shown to be a "spin-blocked" reaction with a high barrier due to the crossing between reactant triplet and product singlet surfaces. In contrast, addition of CO to TpCo(CO) (Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745) is fast because the triplet and singlet surfaces cross at low energy. Particular care is taken to use DFT methods which are in adequate agreement with experimental and high-level computational energetics for these systems.

Introduction

Many reactions of transition metal organometallic compounds involve unsaturated intermediates, reactants, or products, i.e., species with a formal electron count lower than 18. In many cases, 16-electron complexes can exist as either singlet or triplet species, and electronic states corresponding to these different spin pairings often lie rather close in energy. Therefore, it is fairly common to have a reaction that occurs, at least in principle, on multiple potential energy surfaces. The most common example of this in organometallic chemistry is when singlet reactants lead to singlet products but through triplet intermediates. Equally, related cases are known in which stable 16-electron triplet reactants lead to closed-shell products, or indeed in which 15- or 17-electron doublets and quartets are involved. These reactions are referred to as "spin-forbidden" because in the absence of spin−orbit coupling and other such interactions which are not present in the zeroth-order description of molecular electronic structure, changes in spin state do not occur.

The possible effect of such spin state changes on the kinetics of organometallic reactions has long been a matter of debate. In one well-known textbook in the field, it was suggested[1] that spin-forbidden processes might be noticeably slower than analogous spin-allowed ones, a so-called "spin-blocking" effect. However, given the high atomic number of transition metals, especially the heavier second- and third-row elements, relativistic effects, including spin−orbit coupling, should be important for these species. This should alleviate the impact on kinetics of a reaction's spin-forbidden character, or indeed completely remove it. For these reasons, and perhaps also because of the lack of firm experimental evidence, the discussion of spin-blocking was removed from later editions of the above-named textbook. There therefore remains considerable uncertainty in the community concerning the effect on kinetics of spin changes, especially because it is often difficult to define what exactly is meant by an "analogous" spin-allowed reaction, so that comparison can be difficult or impossible. Many reactions are known to occur with a change in spin, but there is little definitive evidence concerning the effect that this has on kinetics.

In recent work,[2] we have shown that the above discussion of how spin state changes may affect kinetics is too simplistic, as it only focuses on one of the two factors involved in establishing the kinetics of such nonadiabatic processes. It is true that surface hopping between zeroth-order potential energy surfaces corresponding to different spin states does not always occur with unit efficiency, and that this can lead to observable dynamical or kinetic effects, even for transition-metal containing systems.[3,4] For example, we have used a nonadiabatic form of transition state theory to compute the rate for addition of carbon monoxide to triplet iron tetracarbonyl to give closed shell Fe(CO)$_5$.[3] This reaction has been found to occur in the gas phase at a rate which is roughly 500 times below that expected from collision theory.[5] We found that the minimum energy crossing point (MECP) between the reactant triplet and product singlet is slightly (0.5 kcal/mol) higher in energy than the reactant asymptote and that

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this accounts for part of the rate reduction. Surface hopping at the MECP, mediated by the spin−orbit coupling matrix element of 66 cm^{-1}, is predicted to occur on average only once out of 20 seam-crossing events, and this also contributes significantly to the low rate.

However, this represents a somewhat special case, in which the reaction is in absolute terms still extremely fast, because the MECP is only just above the reactants' energy level, so that it makes only a modest contribution to the rate reduction. In cases where the spin-induced reaction barrier corresponding to the MECP is larger, the Boltzmann factor it will contribute to the reaction rate will tend to be have a far greater effect on the rate than the nonadiabatic behavior. It is especially important to recognize that even in the limit of strong spin−orbit coupling, and hence fully adiabatic motion through an avoided crossing corresponding to the MECP, a spin change can still have an effect on reactivity, in cases where the avoided crossing between zeroth-order potential energy surfaces leads to a significant energy barrier. "Spin-blocking" of chemical reactions is not purely determined by the strength of spin−orbit coupling.

We have already explored several organometallic[3,6,7] and bioinorganic[8] reactions involving a change in spin and shown how the energy and geometry of the minimum energy crossing points (MECPs) between the relevant potential energy surfaces could be used in qualitative terms to account for reactivity and selectivity.[2] Also, other groups, both before and in parallel with our work, have discussed spin changes in organometallic and other reactions. In some cases, the position of surface crossings has been discussed qualitatively or based on the approximate location of surface crossings,[9] while in others, MECPs have been explicitly located.[10] In the present contribution, we extend our work in this area to address two reactions which have been the focus of considerable interest and which have been used respectively as examples in favor of and against the disputed concept of "spin-blocking" in organometallic chemistry. The first example (Scheme 1a) is oxidative addition of dihydrogen to a tungsten monohydride trisamido complex, [N$_3$N]WH (N$_3$N = [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$),[11,12] which has been put forward as a possible example of the phenomenon of spin-blocking.[12] Thus, unlike many exothermic, irreversible, dihydrogen addition reactions to an unsaturated metal, this reaction is slow, taking 1 day under pressure to proceed to completion.

The other reaction is addition of CO to a triplet tris-pyrazolyl cobalt monocarbonyl, (Tp$^{i-Pr,Me}$Co(CO), where Tp$^{i-Pr,Me}$ =

Scheme 1
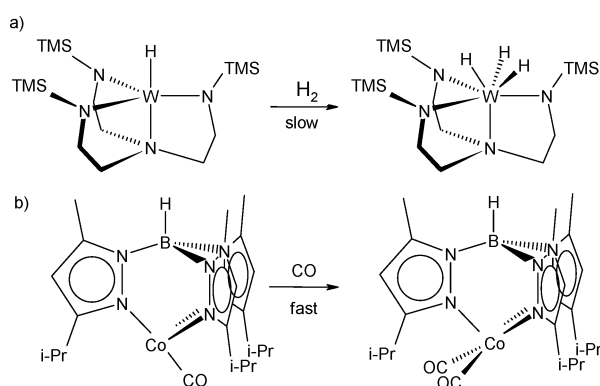
hydrotris(3-isopropyl-5-methylpyrazolyl)borato), see Scheme 1b.[13] This addition reaction is very fast, almost diffusion controlled ($k = 3 \times 10^9$ mol^{-1} L s^{-1}), despite its spin-forbidden nature. The authors concluded that "Based on this observation it is argued that the notion of 'spin-blocking' of organometallic reactions is inappropriate". In other words, this ligand addition process is very similar, in kinetic terms, to other spin-allowed, barrier-free, reactions.

In this work, we report new DFT calculations on the corresponding systems, to show that reactivity in these two high-profile examples can be readily understood in terms of the topology of the potential energy surfaces involved, and in particular of the relative energetics of the reactants, products, intermediates, and MECPs. We also use computation to explain the different reactivity of various small ligands (R$_3$P, CH$_4$, C$_2$H$_4$, CO) with triplet CpCoCO, which has been studied in the gas phase and in solution. In particular, the nonreactivity with alkanes, which contrasts with the ready reactivity observed with the heavier congeners CpRh(CO) and CpIr(CO), has been suggested in a much-cited computational study[14] to be linked to the spin-state change which must occur in the cobalt system. This third system is of further value because it is small enough for us to be able to apply accurate computational techniques and hence calibrate the density functional theory (DFT) methods used for the other, much larger systems shown in Scheme 1. This is particularly valuable for the system of Scheme 1b, as CpCo(CO) is isoelectronic with Tp$^{i-Pr,Me}$CoCO. Our careful calibration of our computations, as well as the use of the "real" systems of Scheme 1, means that computational uncertainties linked to method accuracy or truncation of ligands to give "model" systems are kept to a minimum.

Computational Details

The bulk of the DFT computations have been carried out using the Jaguar program package,[15] together with the standard BP86 and B3LYP functionals. Some additional calculations were carried out using the standard PW91, BPW91, and B3PW91 functionals. Finally, the modified form of the B3PW91 functional, in which the proportion of exact HF exchange has been changed from 20 to 15% (which we[3] refer to as B3PW91*), has also been used for some calculations. Full geometry optimization was carried out for all species. For the transition state (TS) searches we used the quadratic synchronous transit (QST) methods as implemented in the Jaguar program. The MECPs were

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optimized using Jaguar, together with the code developed by one of us.[16,17] Basically, a set of shell scripts and Fortran programs is used to generate Jaguar input, run jobs, extract energies and gradients for both spin states, combine them to produce an effective gradient pointing toward the MECP, update the geometry, and cycle until convergence (energy difference lower than 0.1 mHartree, energy gradient within the seam of crossing within the normal Jaguar convergence criteria). This method is similar to that developed by other groups.[18] In the DFT computations, the metallic atoms were described using the effective core potentials (ECPs) of Hay and Wadt,[19] with the valence and outermost core ($3s^23p^6$ for Co, $5s^25p^6$ for W) electrons described explicitly. This ECP is associated with a TZ basis set (LACV3P), as implemented in Jaguar, with contractions of the form (5s5p5d)/[4s4p3d] for Co and (5s5p3d)/[4s4p3d] for W. We used the standard 6-31G* basis set for B, C, N, O, Si, and H. For this last atom, in some cases indicated below, we added a p-type polarization function (6-31G** basis). Single-point DFT calculations with the larger basis sets discussed below gave energies very close to those obtained with the combination used here. For the large compounds of Scheme 1, vibrational frequency computation is prohibitively expensive, so we cannot include zero-point or thermal corrections. However, for the $CpCo(CO) + CO$ or CH_4 systems, we have computed zero-point energies for most of the stationary points and provide energetics derived both from pure electronic energies and zero-point energy corrected ones; the difference gives a measure of the effect of the latter on energetics.

Additional DFT and coupled cluster single-point calculations were carried out using the MOLPRO 2002.3 package,[20] at the Jaguar/B3LYP-optimized geometry. The CCSD and CCSD(T) computations for singlet states and the RCCSD and RCCSD(T) computations for triplet states, had RHF and ROHF references, respectively. For most of these calculations, we used the standard cc-pVDZ basis set for C, N, O, and H with, for the metallic atoms, flexible basis sets with multiple polarization functions. In particular, for cobalt, we developed for this work two all-electron bases using the Ahlrichs[21] TZV (17s,10p,6d)/[6s,3p,3d] basis set as a starting point. The "BS1" basis is of (18s, 13p,6d,2f,1g)/[8s,7p,4d,2f,1g] size, and the "BS2" one is of (18s, 13p,7d,3f,2g,1h)/[8s,7p,5d,3f,2g,1h] size, and in both cases all other atoms are treated with cc-pVDZ. For some calculations we also used a third set, "BS3", which is the same as BS2 for the cobalt atom but uses the larger cc-pVTZ standard basis on the other atoms. For tungsten, the Stuttgart/Köln group quasi-relativistic ECP[22] was used, with the 5s, 5p, 5d, and 6s electrons described using either a [6s5p4d2f] or a [6s5p4d3f1g] basis set. Full details of these Co and W basis sets are provided in the Supporting Information. In all correlated calculations, the core Co (up to 3s3p), W (up to 5s5p) and C, N and O (1s) orbitals were held frozen.

Results and Discussion

We start by discussing our results obtained for the spin-forbidden ligand addition reactions to the triplet $CpCo(CO)$ system. Carbon monoxide, phosphines, and alkenes are ob-
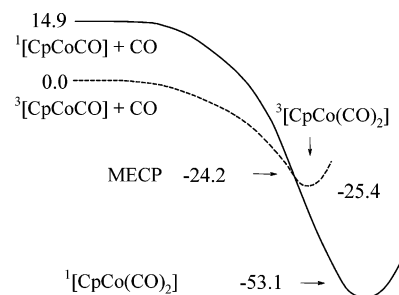

Figure 1. BP86 potential energy profile (in kcal/mol) for the addition of CO to CpCoCO.

served[23] to add very rapidly to this 16-electron fragment, to give saturated singlet species such as $CpCo(CO)_2$. In contrast, unlike the isoelectronic $CpRh(CO)$ and $CpIr(CO)$, $CpCo(CO)$ does not react with alkanes,[24] and there have been suggestions that this difference may be due to the spin state change which would need to occur in this reaction for the cobalt system.[14] Our computed potential energy surfaces enable these different reactivities to be understood.

In Figure 1, the surfaces for addition of CO are shown (see also computed data in Table 1). As in previous studies,[14,25] $CpCo(CO)$ is found to have a $^3A''$ ground state, with a $^1A'$ state lying some 15 kcal/mol higher. In contrast, $CpCo(CO)_2$ is found to have a singlet ground state, bound with respect to the triplet fragments by ca. 50 kcal/mol before correction for zero-point energy. As in the previous study,[14] the *triplet* state of $CpCo(CO)_2$ is found to be bound with respect to fragments, by as much as 25 kcal/mol. There is no barrier to addition of the second CO fragment on the triplet surface, as shown by carrying out a set of constrained geometry optimizations at successively smaller Co–C distances. There is a crossing between the singlet and triplet surfaces in the vicinity of the triplet minimum, with the MECP lying just 1.2 kcal/mol higher in energy than the triplet. In fact, the geometries of the MECP and of triplet $CpCo(CO)_2$ are virtually superimposable, with an rms difference in their Cartesian coordinates of only 0.077 Å. These near-identical geometries are reflected in the bond lengths and angles also; for example, $r(Co–CO)$ is 1.826 Å for the triplet minimum, versus 1.848 Å at the MECP.

The fast addition reaction of CO to $CpCo(CO)$ can be readily rationalized by these potential energy surfaces: addition initially proceeds to give the triplet species, which is strongly enough bound and has a large enough density of rovibrational states, to have a certain lifetime toward dissociation. During this lifetime, the system will cross the energetically very accessible seam of crossing with the singlet surface many times. At each crossing, there will be a certain probability for surface-hopping, and the final result will be formation of the singlet. Loss of excess vibrational energy, ensuring that the adduct does not undergo the reverse of the initial step, loss of CO, can occur by collisional cooling with the background gas as discussed in the experimental paper,[23] in either the triplet or singlet dicarbonyl minima. In this process, the rate-limiting step is the initial addition of the CO molecule, which should occur at a near-gas-collisional rate, given the barrierless triplet potential energy

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Table 1. DFT and CCSD(T) Computed Potential Energies (kcal/mol) for the CpCo(CO) + L (L = CH$_4$, CO) Systems. Numbers in Parentheses Include a Correction for Zero-Point Energy

	DFT					CCSD(T)		
	B3LYP	B3PW91	B3PW91*	BP86	PW91	BS1	BS2	BS3
^{3}[CpCoCO] + L	0.0 (0.0)	0.0	0.0	0.0 (0.0)	0.0	0.0	0.0	0.0
^{1}[CpCoCO] + L	25.7 (25.8)	25.6	22.0	14.9 (14.9)	14.8	18.1	15.4	15.1
CH$_4$ MECP	15.5	14.4	10.1	4.9	2.4			
^{1}[CpCoCO·CH$_4$]	15.4 (17.1)	14.1	8.9	1.6 (3.2)	−1.5			
CH$_4$ ins. TS	27.2 (27.2)	23.3	16.7	6.8 (7.1)	3.8			
^{1}[CpCoCO(CH$_3$)H]	18.8 (19.6)	16.6	10.1	−0.6 (0.5)	−3.1	3.4	1.4	
^{3}[CpCo(CO)$_2$]	−17.9 (−16.7)	−18.7	−20.9	−25.4 (−24.3)	−27.8			
CO MECP	−17.3	−18.2	−20.9	−24.2	−26.9			
^{1}[CpCo(CO)$_2$]	−31.6 (−28.4)	−35.1	−42.1	−53.1 (−49.4)	−56.0	−38.8	−41.3	−41.0

Table 2. DFT Computed Potential Energies (kcal/mol) for the CpCo(CO) + L (L = P(CH$_3$)$_3$, C$_2$H$_4$) System

	B3LYP	BP86
^{3}[CpCoCO] + L	0.0	0.0
^{1}[CpCoCO] + L	25.7	14.9
^{3}[CpCo(CO)P(CH$_3$)$_3$]	−14.4	−17.8
^{1}[CpCo(CO)P(CH$_3$)$_3$]	−20.8	−40.4
P(CH$_3$)$_3$ MECP	−12.2	−17.4
^{3}[CpCo(CO)C$_2$H$_4$]	−7.1	−11.0
^{1}[CpCo(CO)C$_2$H$_4$]	−16.6	−36.8
C$_2$H$_4$ MECP	−5.1	−10.7
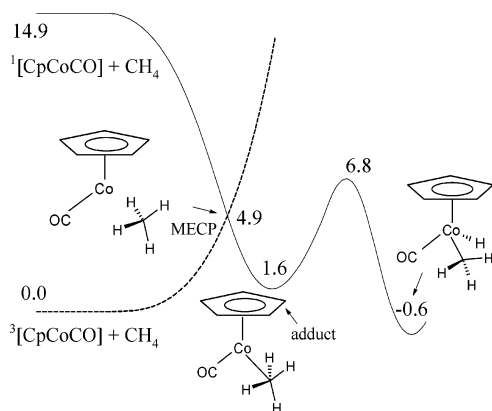
Figure 2. BP86 potential energy profile (kcal/mol) for the insertion of CH$_4$ to CpCoCO.

surface. This is in agreement with the experiment. We have found that the potential energy surfaces for addition of C$_2$H$_4$ and P(CH$_3$)$_3$ have a similar topology, with bound triplet adducts, stable singlet adducts, and very accessible MECPs between the singlet and triplet surfaces lying just above the triplet adduct minima (see Table 2).

The potential energy surfaces for addition of methane are very different, as shown in Figure 2. First, there is no significantly bound minimum on the triplet surface (very weakly bound van der Waals-type complexes, with bond energies of less than 1 kcal/mol, were found at the DFT and CASPT2 levels in ref 14). The second difference concerns the singlet surface. Here, there are two CH$_4$ adducts: In the first, "σ-complex", there is a dative interaction between a doubly occupied orbital on methane and an empty orbital on Co, whereas in the second, formal oxidative addition to give a Co(III) methyl hydride has occurred. In our calculations, these two states are very close in energy and are separated by a modest energy barrier. To rule out different energetics for the cyclohexane reaction, which is the one that has been probed experimentally, the encounter

complex and inserted species have also been located at the BP86 level for this system. The energetics for addition and insertion to form CpCo(CO)(C$_6$H$_{12}$) and CpCo(CO)(H)(C$_6$H$_{11}$), respectively, are very similar to those found for methane addition: +0.3 and −0.9 kcal/mol as compared to +1.6 and −0.6 kcal/mol with methane. The MECP in the methane system between the singlet and triplet surfaces lies ca. 5 kcal/mol above the level of the triplet reactants, i.e., just below the adiabatic C−H bond insertion TS.

Why is no reaction observed between CpCo(CO) and alkanes? The experimental study[24] suggests that the "solvate adduct" (σ-complex) is not formed, and the inserted species certainly is not. Our calculations provide a ready explanation for these observations: it is likely that reaction *does* occur, at least under certain conditions, but that it is reversible and that the products are not stable and hence are not detected. Thus, the MECP does not lie very high in energy, and the probability of crossing from the triplet to singlet surfaces at the MECP would have to be much smaller than the 5% found in the Fe(CO)$_4$ + CO system[3] for reaction to be impossible. As in the Fe(CO)$_4$ case, spin−orbit coupling interactions between singlet and triplet CpCo-(CO) are symmetry allowed, so the coupling matrix element, and hence the hopping probability, is likely to be of the same order of magnitude as that found there. Depending on the degree of spin-forbidden character, either the change of spin at the MECP or the adiabatic insertion TS could represent the overall rate-limiting step for addition but in any case this is expected to be fairly fast. Instead, one can see that *both* adducts, which have roughly the same potential energy as the reactants, are thereby simply not stable enough for addition to be favorable in terms of *free* energy. In rough terms, formation of an adduct from two molecules is disfavored by entropy by ca. 10 kcal/mol at room temperature due to the loss of translational degrees of freedom. Even at the lower temperatures where the attempted reaction was carried out, any addition is likely to be reversible due to the near-thermoneutral character of the addition.

The discussion above revolves around potential energy surfaces computed at the BP86 level of theory. Previous calculations[14] on the CO and CH$_4$ reactions, using DFT and other methods, reach the same conclusion as ours for the CO case, but a very different one for the CH$_4$ reaction. Thus, the PCI-80 parametrized correlation method (based on extrapolation of correlation effects from a MCPF/DZP calculation) judged to be most reliable in that study predicted the insertion product to be as much as 22.9 kcal/mol more stable than the triplet reactants. In that context, of course, thermochemistry could not explain the nonobservation of products which was instead

suggested to be due to the spin state change: it was argued that the crossing between triplet and singlet states would lie at quite high energy (although no MECP was located). Which interpretation is correct? As mentioned in the previous study, different methods yield very different energetics in these systems, in particular for the singlet−triplet state splitting in CpCo(CO), and there is at first sight no particular reason BP86 results should be preferred. This type of problem is common in studies of spin-forbidden reactions in organometallic chemistry and will also affect the results obtained for the Tp[*i*−Pr,Me]Co(CO) system discussed below. We therefore carried out extensive calibration work on CpCo(CO) and some of its reaction products, which we discuss here.

The computed energetics for these species using various different density functional methods are shown in Table 1. As can be seen, very different singlet−triplet state splittings in CpCo(CO), and energetics for addition of CO and CH₄, are obtained using the different functionals. The state splitting follows trends observed before,[3,26,27] with hybrid functionals including larger amounts of "exact" exchange leading to relatively more stable triplets. Bond energies relative to the triplet fragments are therefore also smaller with hybrid functionals. In fact, with the latter, the methane insertion product is predicted to be significantly *higher* in energy than the triplet reactants. Were this description of the CpCo(CO) + CH₄ system correct, then the absence of reaction would be even less surprising than suggested by our preferred BP86 energetics, as shown in Table 1 and Figure 2.

How can one decide which functional gives the better description? As in previous work,[3] we have used accurate CCSD(T) computations using large basis sets to calibrate the DFT methods, and the results are also shown in Table 1. As can be seen by comparing the results obtained using different basis sets, even the largest basis set on Co, roughly of quadruple-ζ quality, does not yield a totally converged result (compare BS1 and BS2 results), but the lighter atom basis sets are nearer convergence (compare BS2 and BS3). As expected, correlation is more important in the singlet state, so that the computed CpCo(CO) singlet/triplet splitting appears to be converging from above, and the value of 15.1 kcal/mol derived from our largest calculations is likely to be an upper bound. The accuracy of our calculations is supported by the fact that the computed first CO bond energy for CpCo(CO)₂ (41.0 kcal/mol, 37.3 kcal/mol after applying the BP86 zero-point energy correction) is in fair agreement with the recent experimental value of 44 ± 1 kcal/mol,[25] the remaining discrepancy with our calculations may reflect the still quite limited basis set.

It is often claimed that the CCSD(T) method cannot give accurate results in first-row transition metal compounds, due to the near-degeneracy effects which occur in these systems, as measured, for example, by the t_1 diagnostic.[28] Following this argument, it is claimed that multireference methods such as CASPT2 should be used instead. However, the results obtained with CASPT2 are highly dependent on the active space used, and it is impossible, or at least very difficult, to use the sort of

balanced active space which includes all zeroth order near degeneracy effects for transition metal compounds other than di- or triatomic radicals.[29] Also, there is little hard evidence that CCSD(T) does indeed give poor results. Indeed, for main-group compounds displaying similar multireference character to the Co compounds in Table 2 (as measured by the t_1 diagnostic, which gives values of 0.05 or lower here), very accurate results can be obtained with CCSD(T).[30]

It should be mentioned that for the present system the PCI-80 results mentioned earlier[14] predict that the inserted methyl hydrido species is significantly more stable than the reactants and thus does not agree with CCSD(T). However, the performance of the PCI-80 method for compounds of the first transition row is less reliable than for second- and third-row systems,[31] because near-degeneracy and correlation effects are stronger, and extrapolation can be hazardous. In this context, we observe that in ref 14 the MCPF calculations themselves, which form the basis for the PCI-80 extrapolation, predict CpCo-(CO) and CpCo(CO)(H)(CH₃) to have almost exactly the same energy, in agreement with our (higher level and larger basis set) CCSD(T) calculations. The PCI-80 discrepancy arises solely upon scaling the MCPF correlation contributions. Although accurate ab initio correlated computations for first-row transition compounds remain difficult, the coupled cluster calculations we report do represent a useful and fairly accurate benchmark.

If we therefore assume that the CCSD(T)/BS3 results of Table 1 are close to being exact, then the BP86 functional can be seen to give the best overall performance, and it is for this reason that we have used this functional to explore the surface-crossing behavior, as discussed above. In particular, given that the singlet−triplet splitting in CpCo(CO) appears to have a maximum value of 15 kcal/mol, whereas all hybrid functionals, including those with a reduced 15% exact exchange contribution, predict much larger splittings, then it appears that "pure" functionals such as BP86 give the best description of spin state energetics in this system. This is rather different to the situation found for some spin-crossover Fe(II) and Fe(III) compounds, for which the best agreement is found with 15% exact exchange.[26] Some evidence has been provided to suggest that this value of 15% is likely to be optimum also for other classes of compounds,[27,32] but unless our CCSD(T) calculations are severely wrong, this does not appear to be the case here. It is worth noting here that for nonmetallic systems B3LYP has been shown to be far more accurate than BP86 (average errors on atomization energies for the G2 dataset are respectively of 2.2 and 10.3 kcal/mol[33]), and it also gives good performance for many transition metal compounds. The results obtained for the one particular case considered here certainly do not constitute a valid reason for using BP86 systematically for transition metal compounds.

We now turn to first of the two larger systems discussed in the Introduction, namely, the triamidotungsten monohydride complex [N(CH₂CH₂NSiMe₃)₃WH] and its reaction with molecular hydrogen.[11,12] The monohydride has been shown experimentally to be paramagnetic, and for symmetry reasons, only

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two of the lone pairs on the amido nitrogens can interact with the metal d orbitals, such that it is formally a 16-electron species, which is best described as a triplet (although strong spin−orbit coupling can be expected for such a heavy element, so that labels of this type are not completely meaningful). Reaction with 1 atm of dihydrogen in benzene occurs slowly at room temperature, over 24 h, to give a thermally stable, diamagnetic trihydride in quantitative yield. The product trihydride is rather stable at room temperature, for example, no H/D redistribution is observed upon stirring the [H,D$_2$] form of the trihydride for 2 weeks.[11]

It is instructive to consider the hydrogen addition reaction in the framework of transition state theory.[34] A rough estimate of the rate constant can be obtained by taking the concentration of H$_2$ in benzene to be constant during the reaction (a large excess was used in the experiment[11]), and for it to be equal to the gas-phase concentration corresponding to a pressure of 1 atm of H$_2$ (0.04 mol/L). Solubility means that the dissolved concentration will actually be somewhat lower, but this effect can safely be ignored for the present qualitative purposes. Complete reaction (roughly 5 half-lives) in 24 h can then be taken to correspond to a second-order rate constant of roughly 0.001 mol^{-1} L s^{-1}. In turn, this corresponds to an activation free energy of 21 kcal/mol. Assuming that the activation entropy for the addition is ca. −29 cal mol^{-1} K^{-1}—as calculated elsewhere for addition of H$_2$ to a ruthenium amido complex[35]— this means that the addition must involve an activation enthalpy of ca. 13 kcal/mol. This estimate depends on many assumptions, so the precise numerical value should not be taken too literally. However, it is clear that the observation of slow (1 day) addition of dihydrogen to the monohydride implies the existence of a significant energy barrier to addition.

Oxidative addition of dihydrogen to unsaturated metal complexes with an empty d orbital should be fast if it is also exothermic. This is because the initial coordination step should be barrierless in such cases, and conversion of the σ-bond complex to the dihydride by insertion into the H−H bond should also be facile[36] (again, provided the dihydride is stable). There are many examples of this behavior. For example, CpRh(CO) readily adds H$_2$ in the gas phase at near collisional rates,[37] and computation has shown that there is no barrier to this reaction.[38] Another example is Ru(dmpe)$_2$, which adds H$_2$ with a rate constant near the diffusion limit.[39] Here too, computation (on Ru(PH$_3$)$_4$) shows that there is no barrier to addition.[40] We note that H$_2$ addition to some 16-electron complexes does involve a barrier, as in the case, e.g., of Vaska complexes IrX(CO)-(PR$_3$)$_2$.[41] However, in these square-planar complexes, there is no low-lying empty metal orbital available for the initial addition step.

Hence the slow reaction in the present addition of H$_2$ to a non-square-planar 16-electron species is somewhat anomalous,

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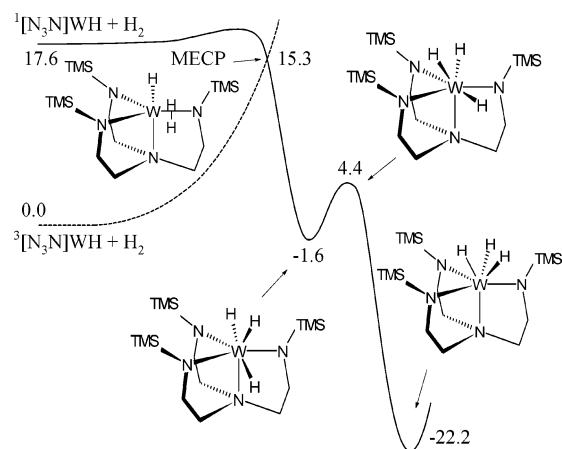(41) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386−&.

Figure 3. BP86 potential energy profile (in kcal/mol) for the insertion of H$_2$ to [N$_3$N]WH.

Table 3. DFT Potential Energies Relative to Triplet Reactants (kcal/mol) for the [N$_3$N]WH + H$_2$ Reaction

	B3LYP	BP86
^{3}[N$_3$N]WH + H$_2$	0.0	0.0
^{1}[N$_3$N]WH + H$_2$	18.9	17.6
^{1}[N$_3$N]W(H)$_3$	−12.2	−22.2
MECP	18.8	15.3
intermediate	8.2	−1.6
transition state	15.2	4.4

and this was remarked on by the authors, who wrote:[12] "Second, it is surprising to us that some relatively simple reactions (e.g. the addition of dihydrogen to [N$_3$N]WH) are so slow". The authors went on to ponder "the possibility that many simple '2-e reactions' are 'spin-blocked' as a consequence of very little of the metal being in the low spin state in which an empty d$_{xz}$ (or d$_{yz}$) and a fully occupied d$_{yz}$ (or d$_{xz}$) orbital are available." However, the full paper describing the reaction[11] contains no such speculation on the origin of the slow nature of the addition, perhaps because of the intervening suggestion[13] that spin-blocking does not occur. Thus the origin of the slow nature of this reaction was unclear.

The computation of singlet and triplet potential energy surfaces for this system allows this question to be resolved. Our results are shown in Figure 3, and in Table 3. First of all, we note that our computed structure for the global minimum in this system, i.e., the trihydride, is in good agreement with the experimental crystal structure[11] (comparative bond lengths and angles are shown in the Supporting Information). The rest of our discussion will therefore focus mainly on energetics. To take the monohydride asymptote first, we find the triplet form to be the ground state, with a state-splitting to the singlet of some 18 kcal mol^{-1}. Unlike in the cobalt systems discussed elsewhere in the paper, this splitting does not depend markedly on the functional used (see Table 3). This is in line with the general observation that spin-state splittings are far less sensitive to the extent of exact exchange admixture for compounds of the metals in the second and third transition rows than for those in the first row.[42] We have also carried out calibration calculations at the CCSD(T) level using polarized basis sets on the model W(NH$_2$)$_3$(NH$_3$)(H)$_n$ systems (n = 1, 3). The results, shown in the Supporting Information, are in good agreement with the BP86 values shown here.

(42) Harvey, J. N. *Struct. Bonding*, in press.

On the singlet surface, the interaction of dihydrogen with the monohydride fragment is almost purely attractive, as shown by a sequence of partial geometry optimizations we have carried out in which the distance between the W atom and the midpoint of the H—H bond is successively constrained to smaller and smaller values. This procedure does predict a very slight barrier (of 1.4 kcal/mol for B3LYP), but this may be an artifact as the preferred orientation of the incoming dihydrogen toward the [N₃N] ligand, and the conformation of the latter, undergo significant changes along the approach coordinate and the partial optimizations are hard to converge. We were also not able to fully optimize a corresponding saddlepoint despite several attempts, which may be either because there is no saddlepoint or because of numerical problems arising from a very small negative curvature along the reaction coordinate (which would be associated with a low barrier). In any case, the *maximum* barrier to addition is very small, as observed in the other cases of addition to unsaturated, low-spin fragments mentioned above.[38,40]

Addition on the singlet surface does not lead directly to the global minimum but to an isomeric trihydride in which the three hydrides are aligned (HWHH dihedral angle close to 180°, see Figure 3). This then undergoes rearrangement over a low barrier to yield the experimentally observed adduct. In summary, the reaction on the singlet surface involves at most a very small barrier and proceeds through an experimentally undetected linear isomer of the adduct, which rearranges over a low barrier to give the products. This potential energy surface is not compatible with the experimental observation that the reaction is slow. This is not surprising as the reactant is the triplet monohydride, not the singlet.

Approaching dihydrogen toward the tungsten center in triplet [N₃N]WH leads to an increase in energy at all distances. This is similar to the behavior upon interaction between methane and triplet CpCo(CO), discussed above. As in that case, there must exist some weakly bonded van der Waals complex between the two fragments, but we have not located this species, as it will in any case not play a role in the kinetics of addition. Instead, the repulsive triplet surface undergoes a crossing with the attractive singlet one, as shown in Figure 3, at a point lying 15.3 kcal/mol above the reactants, i.e., just below the energy of the singlet fragment. The geometry of the MECP, shown schematically in Figure 3, is worthy of some comment. It resembles the intermediate isomer described above but has just one hydride ligand, together with the incoming, slightly elongated (r(H—H) = 0.794 Å), dihydrogen fragment. The forming tungsten—hydrogen bonds have bond lengths r(W—H) of 2.097 and 2.193 Å, compared to 1.740 and 1.728 Å, respectively, in the trihydride intermediate. No MECP was found with a "triangular" geometry similar to that of the global minimum.

We have elsewhere[6] located MECPs for addition of dihydrogen to triplet 16-electron fragments Fe(L)₄ (L₄ = (CO)₄, (CO)₂(PH₃)₂, (CO)₂(dpe), and (PH₃)₄). As in the present case, the triplet surface was found to be repulsive in all cases, and the crossings were found to occur at energies rather similar to those of the excited state iron fragment. The reason for this behavior is the same in all these cases: the triplet surface is repulsive even at quite long range, whereas the singlet surface becomes attractive only upon quite close approach of the
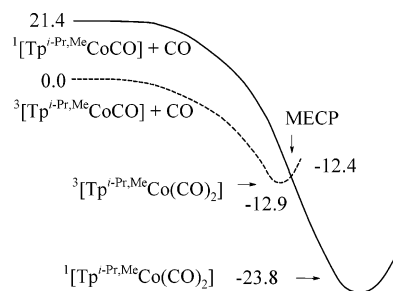

Figure 4. BP86 potential energy profile (in kcal/mol) for addition of CO to Tp$^{i-Pr,Me}$CoCO.

incoming dihydrogen molecule, at which point the triplet state is already significantly destabilized. The reaction of dihydrogen with triplet Fe(CO)₄ has been studied in the gas phase and found to occur well below the gas collision rate.[43] This is consistent with the fact that there is a barrier toward addition induced by the fact that the MECP lies higher in energy than the reactants. This is clearly what is happening in the present case also: addition of H₂ to [N₃N]WH is slow because there is a barrier to addition caused by the need to cross from the triplet to the singlet state. Once the system crosses to the singlet surface, it will form the linear trihydride then rearrange to the observed adduct rapidly. The computed barrier height of 15.3 kcal/mol is in fair agreement with the estimated value of 13 kcal/mol obtained above based on the observed reactivity at room temperature.

However, the "experimental" barrier is obviously not very accurate, and the MECP relative energy is also only a first approximation to the activation barrier. First, of course, the dynamical theory for a spin-forbidden reaction is more complicated than simple transition-state theory, and reactivity will depend to a certain extent on the probability of nonadiabatic surface-hopping at the MECP. This effect, which may lead to an apparent barrier which differs from the energy barrier, has been demonstrated in other cases.[3] However, such effects are quite small, and more important here is that there are considerable uncertainties concerning the accuracy of the DFT potential energy surfaces. Even more critical is that this is an open-shell system containing a very heavy third-row element and the impact of spin—orbit coupling on the computed energetics may well be quite large, at least of the order of a few kcal/mol (see, e.g., ref 44). Near the MECP, for example, extensive mixing between singlet and triplet states will occur such that one may have a nearly adiabatic behavior, with the system crossing a transition state of mixed singlet and triplet nature, lying several kcal/mol below the MECP. For all these reasons, the agreement between experiment and theory can only be approximate. Nevertheless, the computed surfaces clearly show why addition to [N₃N]WH is slow: it *is*, in one sense at least, "spin-blocked"!

If this is the case, why is the other reaction we discuss here, addition of CO to Tp$^{i-Pr,Me}$Co(CO),[13] so fast? This too can be readily explained by considering the computed potential energy surfaces, shown here in Figure 4 and Table 4. As in the tungsten case discussed above, our computed *structures* are in good agreement with experiment (e.g., bond lengths within 0.05 Å,

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Table 4. DFT Potential Energies (kcal/mol) Relative to Reactants for the Reaction [Tp$^{i-Pr,Me}$CoCOl] + CO

	B3LYP	BP86
^{3}[Tp$^{i-Pr,Me}$CoCO] + CO	0.0	0.0
^{1}[Tp$^{i-Pr,Me}$CoCO] + CO	32.9	21.4
^{3}[Tp$^{i-Pr,Me}$Co(CO)$_2$]	−6.5	−12.9
^{1}[Tp$^{i-Pr,Me}$Co(CO)$_2$]	−2.2	−23.8
MECP	0.6	−12.4

angles within 5°). In this case, there are two crystallographical structures to compare with: one is for the diamagnetic dicarbonyl adduct,[13] Tp$^{i-Pr,Me}$Co(CO)$_2$, and one is for a close analogue of the paramagnetic monocarbonyl, Tp^{Np}Co(CO),[45] which has slightly different substituents on the pyrazolyl groups of the Tp ligand. The comparison between our optimized structures and the experimental ones is detailed in the Supporting Information, and we focus instead here on the computed energetics.

As in the CpCo(CO) system, we find a high dependence of the relative spin-state energies on the nature of the functional used, with the hybrid B3LYP functional favoring the triplet Tp$^{i-Pr,Me}$Co(CO) far more over the singlet than does the "pure" BP86 functional. We are unable to calibrate these methods directly in the present case, as the system is too large. However, the good agreement between CCSD(T), BP86, and experiment for the isoelectronic CpCo(CO) system suggest that BP86 should perform well here also. There is one valuable element of experimental data available for the Tp$^{i-Pr,Me}$Co(CO) system, namely, the enthalpy change associated with addition of the second carbonyl, which was found to be −12.9 kcal/mol (note that the measured entropy change of −32 cal mol^{-1} K^{-1} is in line with expectations for a bimolecular process of this type, which indicates that the enthalpy is likely to be very accurate). As in the CpCo(CO) case, BP86 is in qualitative agreement with the experimental value, although, again as in that case, the computed value of the second bond energy is somewhat too large. Part but not all of the error is due to our inability (for reasons of computational expense) to compute vibrational frequencies and hence a zero-point energy correction to the bond energy in this large system. In any case, the BP86 results are of a satisfactory quality for the purposes of this work, and it is worth noting that they are in much better agreement with experiment than the B3LYP ones, which predict Tp$^{i-Pr,Me}$Co(CO)$_2$ to have a *triplet* ground state, with a tiny bond energy for the singlet state.

Two important new features, with respect to what was known from experiment, are also shown in Figure 4 and Table 4. First, as well as a stable singlet adduct, Tp$^{i-Pr,Me}$Co(CO)$_2$ has a triplet state which is bound with respect to loss of carbonyl. Despite its high-spin, 18-electron nature, this state does not involve a change in coordination of the other ligands, but many of the bonds are somewhat elongated with respect to the singlet minimum (e.g., r(Co−C) = 1.857 vs 1.731 Å, and r(Co−N) = 2.191, 2.169 and 2.076 Å vs 2.121, 2.008 and 2.002 Å). This is similar to what we found for the CpCo(CO)$_2$ system, and as there, we have confirmed by carrying out partial geometry optimizations at successively smaller values of r(Co−C) that addition of the second carbonyl to triplet Tp$^{i-Pr,Me}$Co(CO) is a

barrierless process. Next, the singlet and triplet surfaces of Tp$^{i-Pr,Me}$Co(CO)$_2$ cross very close in energy to the triplet dicarbonyl minimum. The geometry of this MECP is mostly unremarkable, as it corresponds to a slight shift of the triplet geometry toward the singlet one (e.g., r(Co−C) = 1.832 Å in the MECP vs 1.857 Å in the triplet).

Fast addition of CO to Tp$^{i-Pr,Me}$Co(CO) is readily explained in the context of these potential energy surfaces. Thus, barrierless and hence near-diffusion-controlled addition will occur on the triplet surface. During its short lifetime on the triplet potential energy surface, the adduct will repeatedly pass the crossing seam with the singlet surface, and each passage will be accompanied by a significant probability for hopping to the singlet, such that production of the latter, experimentally observed, product will dominate over the competing loss of carbonyl. Even if the triplet species becomes collisionally cooled, its thermal motion will constantly lead it to the vicinity MECP, so that it will relax rapidly to the singlet. It is therefore not surprising that the triplet adduct itself has not been observed.

Conclusions

The theory of nonadiabatic processes is well understood in physical chemistry, in terms of zeroth-order potential energy surfaces and the couplings between them. In practice, the act of passing from one surface to another tends to be dominated by events occurring in regions where the two corresponding potential energy surfaces approach each other closely. This account provides a useful framework for discussing the impact of spin state changes upon the rates of organometallic reactions. In the preceding section, we presented new computational results concerning a number of spin-forbidden reactions of CpCo(CO), and for H$_2$ and CO addition to [N$_3$N]WH and Tp$^{i-Pr,Me}$Co(CO), respectively. We have located the MECPs between high spin and low spin surfaces, and thereby are able to discuss the topology not only of the individual surfaces but also of the regions where they cross and hence where spin changes must occur. In all cases, the relative energy of the MECPs, together with the other computed features of the potential energy surfaces, enable the observed experimental reactivity to be explained.

To reach reliable conclusions in this study, one important technical requirement has been the ability to locate surface crossings (MECPs),[17] which have not been considered before for any of these systems and certainly not for the rather large species in Scheme 1. Almost as important was to select a computational level cheap enough to carry out geometry optimization, and in particular MECP optimization, yet accurate enough compared to experimental benchmarks. In recent years, DFT has become very popular among inorganic and organometallic chemists because it is relatively affordable, yet yields many accurate results, especially with the B3LYP functional which has been applied successfully to a remarkably large number of systems and yields excellent energies for the G2 benchmark set of compounds.[33] At the same time, some theoretical chemists have become increasingly critical of DFT due to the many shortcomings it displays[46] and the perceived ad hoc character of the modifications which are being proposed in order to make functionals more accurate.[47] It is easy to

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sympathize with this view, given the dramatically different computed energetics derived for the some of the systems here with two very common functionals, B3LYP and BP86 (see, e.g., Tables 1 and 4). Nevertheless, the optimized *geometries* are in much better agreement, and with careful attention to experimental and computational benchmarks, it is possible to identify functionals which perform adequately well *for a given system*, although not necessarily for all others.[48]

The first system considered is triplet CpCo(CO); this undergoes rapid addition of species such as ethene, carbon monoxide, and trimethylphosphine. The reason for the fast reactivity is that these molecules are relatively strong-field ligands and are thereby able to coordinate to high-spin CpCo(CO) in an exothermic way. The resulting CpCo(CO)(L) intermediate, while violating the 18-electron rule given its high-spin nature, is more stable than the separated fragments because the new bond formed with the incoming ligand is strong enough to offset the partial loss of bonding to the existing ligands. In all three cases, low-lying MECPs between the triplet and singlet surfaces are found in the vicinity of the triplet minimum, such that conversion to the more stable singlet adduct should be easy.

Addition of alkanes to CpCo(CO) is not observed, although they do add to CpRh(CO) and CpIr(CO). It has been suggested in the literature that this difference is due to the triplet nature of CpCo(CO).[14] However, our conclusion is that it is more likely to be associated with the thermoneutral and hence endoergic nature of the addition reaction. Alkane solvates or products of oxidative insertion into C−H bonds may in fact form, based on our calculations, as there is only a small spin-change induced barrier (and, for the latter, a low-lying insertion TS) separating them from the reactants. However, they are then likely to undergo the reverse process under most conditions.

The next example appears to be a genuine case of spin-blocking, although the origin of this rate reduction is not linked to the strength of spin−orbit coupling but to the topology of the potential energy surfaces involved. Thus, dihydrogen addition to [N₃N]WH is anomalously slow, and our calculations suggest that this is due to the occurrence of a significant spin change-induced barrier along the reaction coordinate for oxidative addition. Unlike the CO, ethene, and phosphine molecules, but like methane, H₂ is a very poor ligand and hence does not bind exothermically to 16-electron triplet fragments. The small gain in energy expected from forming an interaction with these fragments would be more than offset by the destabilization associated with the electronic reorganization, and loss of binding to the other ligands, which would have to occur. [This

contrasting behavior between strong and weak field ligands during addition to high-spin metal centers was first noted and rationalized in studies of dinitrogen and carbon monoxide addition to an unsaturated molybdenum comples (Keogh, D. W.; Poli, R. *J. Am. Chem. Soc.* **1997**, *119*, 2516−2523).] As in the methane + CpCo(CO) case, then, there is an energy barrier to addition arising from the crossing between the repulsive triplet and attractive singlet potential energy surfaces. For H₂ + [N₃N]-WH, this barrier is substantial and accounts for the observed slow reaction. There is a pleasing if fortuitous agreement between the computed barrier height and the one estimated from the experimental data.

Finally, CO addition to Tp$^{i-Pr,Me}$Co(CO) is predicted to be fast for the same reasons as discussed for ligand addition to CpCo(CO): the strong CO ligand can add in a barrier-free, exothermic way to the triplet metal species. There is then a low-lying MECP which mediates conversion to the observed singlet product.

In overall conclusion, spin-blocking is indeed a legitimate concept, and some reactions, of which one noteworthy example is discussed here, are significantly slower compared to analogous spin-allowed reactions because of spin blocking. However, the impact on reaction rates depends strongly on the details of the potential energy surfaces and of the topology associated with their crossing. Many spin-forbidden reactions proceed as fast as other, "normal" reactions. Although the qualitative model used here to account for the attractive or repulsive shape of the interaction between high-spin metallic fragments and incoming ligands may enable one to predict roughly when spin-blocking will occur and when it will not, it is clearly not possible to generalize to all spin-forbidden processes. So, *can* spin state change slow organometallic reactions? It depends...

Supporting Information Available: Details of basis sets used in correlated calculations on Co and W compounds. Selected optimized geometric parameters, with comparison to experiment in some cases, for CpCo(CO)(CH₃)(H), W[N₃N]H₃, and TpCo-(CO)$_n$ ($n = 1, 2$), results of calibration calculations on W(NH₂)₃-(NH₃)(H)₃, and Cartesian coordinates for stationary points relating to the CpCo(CO), TpCo(CO), and W[N₃N]H reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(48) We do not claim that the BP86 functional, which is much less accurate than B3LYP for the G2 benchmark systems, should be used in preference to it in other cases without careful calibration.