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Steric Effect of Phosphorus Ligands on Fe(CO)$_4$(P donor) and Ru$_3$(CO)$_9$(P donor)$_3$ Photocatalyzed 1-Pentene Isomerization

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Photoexcitation at 355 nm of $[Fe(CO)_4L]$ and $[Ru_3(CO)_9L_3]$ (L = CO, PPh_3, $P(OMe)_3$, and P(O-*o*-tolyl)$_3$) can be used to generate catalysts for the isomerization of 1-pentene to *cis*- and *trans*-2-pentene. Each complex gives a different initial ratio of *trans*- to *cis*-2-pentene ranging from approximately 6 for $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_9(P(OMe)_3)_3]$ to approximately 1 for [Fe(CO)$_4$P(O-*o*-tolyl)$_3$]. Comparisons of the initial ratios of the isomeric products shows that steric effects, not electronic effects, of the P-donor ligands are responsible for the variation in isomer ratio. The more sterically demanding complexes give the smallest ratio of *trans*- to *cis*-2-pentene. Thus, sterically crowded complexes give enrichment of the less thermodynamically stable alkene. Similarly, beginning with *cis*-2-pentene, $[Fe(CO)_3(PPh_3)_2]$ gives a much smaller ratio of *trans*-2-pentene to 1-pentene at low conversion than does $[Fe(CO)_5]$ under 355-nm irradiation. Initial quantum yields for isomerization generally exceed unity, and the ultimate distribution of alkenes is the thermodynamic ratio, evidencing the photochemical formation of a thermally active catalyst. For $[Fe(CO)_4L]$ the only detected primary photoprocess is dissociative loss of CO with a quantum yield of ~0.4, while for $[Ru_3(CO)_9L_3]$ the primary photoprocess is proposed to be rupture of a metal–metal bond.

Introduction

In homogeneous catalysis it is well established that the ligands in the coordination sphere of a metal-centered catalyst during the actual catalytic reaction can influence the rate and product distribution of the reaction.[1] This effect of the ligands may be divided into steric and electronic effects. One class of ligands that has been studied in this regard is the phosphorus ligands. These ligands are ideal for two reasons: (1) they are capable of stabilizing many complexes[2] (e.g., metal alkyls and metal hydrides) that are important in homogeneous catalytic systems and (2) a vast number of phosphorus ligands exhibiting a wide range of steric and electronic properties are known.[3] The steric and electronic properties of many phosphorus ligands have been quantified and tabulated by Tolman.[3b] Examples of phosphorus ligands influencing the rate and/or product distribution of a reaction by primarily steric[4] or electronic[4b,5] effects are known, but in other cases the nature of the ligand effect is ambiguous.[6] Perhaps the two most significant contributions of phosphorus ligand effects have been realized in the rhodium-catalyzed hydroformylation of olefins[4a,7] and in the rhodium catalyzed asymmetric synthesis of *l*-DOPA.[8] In both cases optimal results are obtained primarily by altering the structural properties of the phosphorus ligands bonded to the metal center.

In the course of our work on the photocatalyzed 1-pentene isomerization using mono- and trinuclear iron and ruthenium complexes, we noted that the initial catalysis product ratio is dependent on the catalyst precursor used.[9] Further investigation showed that this ratio would vary simply by varying the phosphorus ligand bonded to the catalyst precursor. This afforded us an opportunity to examine the effect of the phosphorus ligand on the course of this reaction. No such investigation into the factors affecting product distributions has been done with any photocatalytic system. Herein, we report our results concerning the photocatalyzed isomerization of 1-pentene using the catalyst precursors, $[Fe(CO)_4L]$ and $[Ru_3(CO)_9L_3]$ (L = CO, PPh_3, $P(OMe)_3$, and P(O-*o*-tolyl)$_3$).

Experimental Section

Materials. All solvents were reagent grade and distilled under Ar from CaH_2 or sodium benzophenone ketyl. The 1-pentene (99.9%) was obtained from Chemical Samples Co. and passed through Al_2O_3 prior to use. The *n*-hexane (99+%) and PPh_3 were obtained from Aldrich Chemical Co. and purified by distillation and recrystallization, respectively. The $P(OMe)_3$ (distilled prior to use) and P(O-*o*-tolyl)$_3$ (used as received) were obtained from Strem Chemical, Inc. The $[Ru_3(CO)_{12}]$ obtained from Strem

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Chemicals, Inc., was recrystallized, and the [$Fe(CO)_5$] obtained from Pressure Chemicals was passed through Al_2O_3 prior to use. The [$Ru_3(CO)_9L_3$][10] and [$Fe(CO)_4L$][11] complexes (L = PPh_3, $P(OMe)_3$, and P(O-*o*-tolyl)$_3$) were prepared according to known literature methods and characterized by standard spectroscopic techniques.

Instrumental. All vapor-phase chromatography (VPC) was done with the use of a Varian Series 1440 or 2440 gas chromatograph equipped with flame ionization detectors and a Varian A-25 strip chart recorder or a Hewlett-Packard 3380S integrator. Separation of linear pentenes was accomplished on a 30 ft × $^1/_8$ in. column of 20% propylene carbonate on Chromosorb P at 25 °C. All infrared spectra were recorded with the use of matched path length (0.1 or 1.0 mm) NaCl solution cells and a Perkin-Elmer Model 180 grating infrared spectrometer. All electronic absorption spectra were recorded with the use of a Cary 17. The irradiation source for 355-nm light (width at half-height of ~15 nm) was two 15 W General Electric blacklight bulbs (~10^{-6} einstein/min). Light intensity was determined by ferrioxalate actinometry.[12]

Catalysis Procedure. Generally, a benzene solution 10^{-3} M in catalyst precursor, 1.76 M in 1-pentene, and 0.1 M in *n*-hexane was prepared. One-milliliter aliquots of this solution and 2 × 7 mm magnetic stir bars were placed into Pyrex test tubes (13 × 100 mm) with constrictions, degassed by five freeze-pump-thaw cycles, and hermetically sealed. The stirred samples were irradiated with the 355-nm light source. The samples were air-cooled to ensure they remained at room temperature. Thermal controls (foil wrapped ampules containing the catalysis solutions) were placed next to the samples being photolyzed. Light intensities of 10^{-6} einstein/min were determined by ferrioxalate actinometry,[12] and the solutions were analyzed by VPC following the reaction. The same procedure was used for neat 1-pentene solutions that were 2 × 10^{-3} M in iron catalyst precursor.

Photochemistry of $Fe(CO)_4L$ (L = PPh_3, and P(O-*o*-tolyl)$_3$). A benzene solution ~5 × 10^{-3} M in [$Fe(CO)_4L$] and 0.1 M in the appropriate phosphorus ligand, L′ (L′ = PPh_3, $P(OMe)_3$, and P(O-*o*-tolyl)$_3$), was prepared. Three-milliliter aliquots of this solution were placed into Pyrex test tubes (13 × 100 mm) with constrictions, degassed by five freeze-pump-thaw cycles, and sealed hermetically. Near-UV, 355-nm, irradiation of the solutions yields initially [$Fe(CO)_3(L)(L')$] by IR spectral measurements.[9,15] The appropriate thermal controls show no reaction on the same time scale as the photoreactions. The 366-nm reaction quantum yield for the reaction of [$Fe(CO)_4PPh_3$] in the presence of 0.1 M PPh_3 was determined by irradiation of the ampules in a merry-go-round[13] equipped with a 550-W Hanovia medium-pressure mercury lamp filtered with Corning filters 0-52 and 7-37 to isolate the 366-nm emission. The light intensity (~10^{-7} einstein/min) was determined by ferrioxalate actinometry.[12]

Photochemistry of [$Ru_3(CO)_9L_3$] (L = $P(OMe)_3$ or P(O-*o*-tolyl)$_3$). A benzene solution ~5 × 10^{-3} M in [$Ru_3(CO)_9L_3$] and 0.1 M in L was prepared. Three-milliliter aliquots of this solution were placed into Pyrex text tubes (13 × 100 mm) with constrictions, degassed by five freeze-pump-thaw cycles, and sealed hermetically. Near-UV, 355-nm, irradiation of the solutions yielded [$Ru(CO)_3L_2$] by IR spectral measurements.[9]

Results and Discussion

Previous studies of photocatalyzed reactions using iron and ruthenium carbonyl catalyst precursors show that the ratio of catalysis products depends on the catalyst precursor used and can give information concerning the actual catalytically active species.[9,14] In particular, the initial ratio of *trans*- to *cis*-2-pentene obtained in the photocatalyzed 1-pentene isomerization was about 60% lower when using the [$Fe(CO)_4PPh_3$] precursor as opposed to [$Fe(CO)_5$].[9b] Similar results were observed with [$Ru_3(CO)_{12}$] and [$Ru_3(CO)_9(PPh_3)_3$]. A key question is whether the effect of the phosphorus ligand is due to the electronic or steric properties of the ligand. A comparison of the photocatalytic activity of [$Fe(CO)_4L$] and [$Ru_3(CO)_9L_3$] (L = CO, PPh_3, $P(OMe)_3$, and P(O-*o*-tolyl)$_3$) can answer this. The $P(OMe)_3$ and P(O-*o*-tolyl)$_3$ ligands are fairly similar electronically, both less basic than PPh_3, whereas the PPh_3 and P(O-*o*-tolyl)$_3$ ligands are sterically similar, both having larger cone angles than $P(OMe)_3$.[3b] This choice of complexes should enable us to differentiate between the steric and electronic effects of the phosphorus ligands on the product distribution of the photocatalyzed 1-pentene isomerization. The electronic and steric parameters of the phosphorus ligands are shown in Table I. Unfortunately, the electronic properties of P(O-*o*-tolyl)$_3$ and $P(OMe)_3$ are not identical. However, we note that it is the sterically larger that is the best π acceptor and hence electronically would be more like CO, the least sterically demanding ligand. In the complexes studied the CO stretching absorptions are invariably slightly higher in energy for the P(O-*o*-tolyl)$_3$ than for the analogous $P(OMe)_3$ complexes, cf. Table II, establishing the P(O-*o*-tolyl)$_3$ to be more CO-like than $P(OMe)_3$ with respect to electronic factors. It is clear that P(O-*o*-tolyl)$_3$ is significantly more structurally demanding than $P(OMe)_3$ or CO. Before the catalysis results are discussed, the photochemistry of the iron and ruthenium systems should be delineated.

Table I. Steric and Electronic Parameters of Phosphorus Ligands[a]

L, phosphorus ligand	θ,[b] deg	ν,[c] cm^{-1}
$P(OMe)_3$	107	2079.5
P(O-*o*-tol)$_3$	141	2084.1
PPh_3	145	2068.9

[a] Values obtained from ref 3b. [b] The steric parameter (cone angle), as determined by Tolman,[3b] is the apex angle of a cylindrical cone, centered 2.28 Å from the center of the P atom, which just touches the van der Waals radii of the outermost atoms of the CPK molecular model of the ligand. [c] The electronic parameter, as determined by Tolman,[3b] is the frequency of the A_1 carbonyl mode of $Ni(CO)_3L$ (L = phosphorus ligand) in CH_2Cl_2. This band is measured with an accuracy of ±0.3 cm^{-1}.

Photochemistry of $Fe(CO)_4L$. Near-UV, 355-nm, irradiation of [$Fe(CO)_4PPh_3$] in the presence of 0.1 M PPh_3 yields [$Fe(CO)_3(PPh_3)_2$] (ν_{CO} = 1885 cm^{-1}).[9] Infrared band positions for all relevant complexes are given in Table II. Photolysis of [$Fe(CO)_4PPh_3$] in the presence of 0.1 M $P(OMe)_3$ produces [$Fe(CO)_3(PPh_3)(P(OMe)_3)$] ($\nu_{CO}$ = 1898 cm^{-1}) and not [$Fe(CO)_4P(OMe)_3$] (ν_{CO} = 2063, 1992, 1963, and 1951 cm^{-1}) or [$Fe(CO)_3(P(OMe)_3)_2$] (ν_{CO} = 1920 and 1912 cm^{-1}).[15] Thus, the primary photoreaction for [$Fe(CO)_4PPh_3$] is loss of CO with a 366 nm quantum yield of 0.4 ± 0.04 (eq 1). This parallels the photochemistry observed for the [$Ru(CO)_4PPh_3$] complex.[9a] Photolysis of [$Fe(CO)_4P(OMe)_3$] in the presence of 0.1 M PPh_3 yields [$Fe(CO)_3(PPh_3)(P(OMe)_3)$], and near-UV, 355-nm, irradiation of [$Fe(CO)_4$P(O-*o*-tolyl)$_3$] (ν_{CO} = 2065, 1995, 1965, and 1959 cm^{-1}) in the presence of 0.1 M PPh_3 yields apparently [$Fe(CO)_3(PPh_3)$P(O-*o*-tolyl)$_3$] (ν_{CO} = 1905 cm^{-1}). No [$Fe(CO)_4PPh_3$] was detected in either reaction. The

$$[Fe(CO)_4PPh_3] \xrightarrow[\Phi\,=\,0.4\,\bullet\,0.04]{h\nu,\ 366\ \text{nm}} [Fe(CO)_3PPh_3] + CO \quad (1)$$

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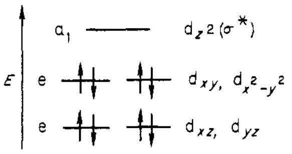
Table II. Infrared Band Positions in CO Stretching Region for Relevant Complexes at 25 °C

complex	solvent	band positions, cm^{-1}
$Fe(CO)_5$	isooctane	2022, 2000
	1-pentene	2023, 2000
$Fe(CO)_4(PPh_3)$	benzene	2049, 1973, 1939
	isooctane	2054, 1978, 1942
$Fe(CO)_4(P(OMe)_3)$	benzene	2060, 1986 (1951, 1944)^a
	isooctane	2060, 1992 (1962, 1950)^a
$Fe(CO)_4(P(O\text{-}o\text{-}tolyl)_3)$	benzene	2064, 1992 (1960, 1955)^a
	isooctane	2065, 1995 (1965, 1959)^a
$Fe(CO)_4$(1-pentene)	isooctane	2081, 1978 (other bands obscured by $Fe(CO)_5$)
	1-pentene	2082, 1978 (other bands obscured by $Fe(CO)_5$)
$Fe(CO)_4$(*cis*-2-pentene)	isooctane	2077, 1995, 1973
$Fe(CO)_4$(*trans*-2-pentene)	isooctane	2079, 1997, 1975
$Fe(CO)_3(PPh_3)_2$	benzene	1885
	isooctane	1893
$Fe(CO)_3(P(OMe)_3)_2$	benzene	(1920, 1912)^a
$Fe(CO)_3(PPh_3)(P(OMe)_3)$	benzene	(1899, 1892)^a
$Fe(CO)_3(PPh_3)(P(O\text{-}o\text{-}tolyl)_3)$	benzene	(1907, 1903)^a
$Fe(CO)_3(PPh_3)$(1-pentene)	benzene	2011, 1944, 1916
$Fe(CO)_3(P(OMe)_3)$(1-pentene)	isooctane	2025, ~1961, 1930
$Fe(CO)_3(P(O\text{-}o\text{-}tolyl)_3)$(1-pentene)	isooctane	~1968
$Ru(CO)_3(PPh_3)$(1-pentene)^b	1-pentene/benzene	2033, 1976, ~1950^b
$Ru(CO)_3(P(OMe)_3)_2$	benzene	(1924, 1915)^a
$Ru(CO)_3(P(O\text{-}o\text{-}tolyl)_3)_2$	benzene	(1926, 1917)^a
$Ru(CO)_3(PPh_3)_2$	benzene	1895
$Ru_3(CO)_{12}$	isooctane	2061, 2031, 2012
$Ru_3(CO)_9(PPh_3)_3$	CH_2Cl_2	2046, 2022, 1982, 1975, 1950 sh
$Ru_3(CO)_9(P(OMe)_3)_3$	CH_2Cl_2	2057, 1992, 1982, 1958
$Ru_3(CO)_9(P(O\text{-}o\text{-}tolyl)_3)_3$	CH_2Cl_2	2060, 2006, 1992, 1975

[a] Broad feature, slightly split with approximate maxima given. [b] Generated by purging out CO with N_2 while irradiating $Ru(CO)_4PPh_3$ in 7.8 M 1-pentene in benzene. The lowest absorptions are obscured by the absorption of $Ru(CO)_4PPh_3$ at 1952 cm^{-1}.

Scheme I. d Orbital Diagram for $Fe(CO)_4L$ Complexes



quantum yields for CO dissociation from $[Fe(CO)_4P(OMe)_3]$ and $[Fe(CO)_4P(O\text{-}o\text{-}tolyl)_3]$ have not been determined quantitatively but are similar to that found for $[Fe(CO)_4PPh_3]$. The products *trans*-$[Fe(CO)_3LL']$ formed from irradiation of $[Fe(CO)_4L]$ in the presence of L′ appear to be initially formed quantitatively, based on disappearance of starting material. The broad prominent infrared absorption in the CO stretching region is consistent with the trans arrangement of L and L′.[9,15] No other metal-containing products are detectable by infrared and, in particular, we note that there is no loss of L from $[Fe(CO)_4L]$ to form $[Fe(CO)_4L']$ in the presence of L′ for the systems studied. All data are for conversion of <20%.

The observed photochemistry of the $[Fe(CO)_4L]$ complexes logically results from ligand field excited states involving the population of the σ-antibonding d_{z^2} orbital,[16] since the Fe(0) complexes have the d orbital diagram represented by Scheme I. All of the $[Fe(CO)_4L]$ complexes have the same geometrical structure and belong to the C_{3v} point group, and the donor atoms are all the same. The $[Fe(CO)_4L]$ complexes only show tail absorption in the near-UV, and no well-defined band can therefore be attributed to the $e \rightarrow a_1$ transitions. However, the dissociative loss of CO is an unambiguous result empirically, and an expected finding. The surprising finding perhaps is that the quantum yield for loss of L, particularly L = phosphite, is insignificant. Since the phosphite ligands are on the z axis and have CO-like properties and the d_{z^2} orbital is principally σ antibonding along the z axis, the lack of P-donor loss is surprising. However, the photoinert Fe–P bond is what allows an investigation of the P-donor structural effects, since the P donor must, presumably, remain in the coordination sphere to exert effects on the distribution of catalytic products. Note that the photochemistry only establishes that the excited state does not detectably lose the P-donor ligand. That the P donor remains bound during the (thermal) catalytic chemistry that occurs after CO loss is demonstrated by the different ratio of initial catalytic products as L is varied (*vide infra*).

Finally, concerning the photochemistry of $[Fe(CO)_4L]$ it is noteworthy that 355-nm irradiation in the presence of 1-pentene yields infrared detectable but very thermally (25 °C) substitution labile, 1-pentene complexes (eq 2).

$$[Fe(CO)_4L] \xrightarrow[\text{1-pentene}]{h\nu} [Fe(CO)_3L(\text{1-pentene})] + CO \qquad (2)$$

Infrared data in the CO stretching region are included in Table II. The noteworthy finding is that for L = PPh_3 and $P(OMe)_3$ there are three infrared bands consistent with a cis disposition of the alkene and the P donor. However, for L = $P(O\text{-}o\text{-}tolyl)_3$ there is only one band, consistent with a trans arrangement of the P donor and the alkene. This result alone clearly establishes a basis for the assertion that the nature of the P donor can significantly alter the catalytic chemistry in these photochemical systems. But notice here that PPh_3, having a slightly larger cone angle that the $P(O\text{-}o\text{-}tolyl)_3$, gives a cis complex whereas the $P(O\text{-}o\text{-}tolyl)_3$ gives trans. There is clearly a role for both electronic and geometric structure effects from L on the nature of the alkene complexes, as is almost always the case in attempts to separate electronic and steric effects on chemical reactivity.

Photochemistry of $Ru_3(CO)_9L_3$. Photolysis of $[Ru_3(CO)_{12}]$ in the presence of CO or 1-pentene results in fragmentation of the cluster with a quantum yield of ~

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[16] Dartiguenave, M.; Dartiguenave, Y.; Gray, H. B. *Bull. Chim. Soc. Fr.* **1969**, *12*, 4223.

10^{-2}, as shown in eq 3.[14,17] The irradiation of $[Ru_3(CO)_9(PPh_3)_3]$ in the presence of CO or PPh_3 yields $[Ru(CO)_4PPh_3]$ or $[Ru(CO)_3(PPh_3)_2]$, respectively, also with low quantum efficiency.[9a] In both cases optical excitation results in the population of an orbital which is strongly σ antibonding with respect to the Ru–Ru bonds.[18] The reactions are though to proceed via photoinduced metal–metal bond homolysis, generating a tethered diradical species which subsequently thermally fragments into mononuclear species.[9a,14,17c] Consistently, optical excitation of $[Ru_3(CO)_9(P(OMe_3)_3]$ in the presence of 0.1 M $P(OMe)_3$ yields $[Ru(CO)_3(P(OMe)_3)_2]$ (ν_{CO} = 1924 and 1915 cm^{-1}), and irradiation of $[Ru_3(CO)_9(P(O\text{-}o\text{-tolyl})_3)_3]$ in the presence of 0.1 M $P(O\text{-}o\text{-tolyl})_3$ yields $[Ru(CO)_3(P(O\text{-}o\text{-tolyl})_3)_2]$ (ν_{CO} = 1926 and 1917 cm^{-1}). The $[Ru(CO)_3L_2]$ products have infrared spectra consistent with a trans arrangement of the two L's and are clearly derivatives of the known PPh_3 species.[9a] The yield of $[Ru(CO)_3L_2]$ from irradiation of $[Ru_3(CO)_9L_3]$ in the presence of L is initially quantitative based on infrared spectral measurements. Although the quantum yields of these latter two reactions have not been determined, both reactions are qualitatively quantum inefficient. The photofragmentation of these clusters is expected to occur by the same mechanism proposed for $[Ru_3(CO)_{12}]$ and $[Ru(CO)_9(PPh_3)_3]$.

$$[Ru_3(CO)_{12}] \xrightarrow[L = CO,\ alkene]{h\nu} 3[Ru(CO)_4L] \qquad (3)$$

The irradiation of the $[Ru_3(CO)_9L_3]$ complexes can be carried out by using visible light, since these complexes have an intense ($\epsilon \approx 10\,000\ M^{-1}\ cm^{-1}$) absorption band at about 500 nm. The first band position varies with L in the following manner: L = CO, λ_{max} = 396 nm; L = $P(OMe)_3$, λ_{max} = 431 nm; L = $P(O\text{-}o\text{-tolyl})_3$, λ_{max} = 444 nm; and L = PPh_3, λ_{max} = 506 nm. Near-UV and visible excitation give nearly the same quantum yields. Interestingly, visible light (514.5 nm from an Ar ion laser) photoexcitation of the $[Ru_3(CO)_9L_3]$ complexes in the presence of 1.76 M 1-pentene does not lead to rapid loss of the Ru complexes except for L = CO. The quantum yield for disappearance of $[Ru_3(CO)_9L_3]$ where L = PPh_3 is $<10^{-4}$, and there are no alkene products detected by infrared. It appears that mononuclear $[Ru(CO)_4PPh_3]$ and $[Ru(CO)_3(PPh_3)_2]$ are formed slowly. Similarly, irradiation of $[Ru(CO)_4PPh_3]$ that is known to yield dissociative loss of CO[9] does not lead to the build-up of the expected $[Ru(CO)_3(PPh_3)(1\text{-pentene})]$ when the irradiation is carried out in the presence of high concentrations of 1-pentene in sealed reaction vessels. Under the same conditions $[Fe(CO)_3(PPh_3)(1\text{-pentene})]$ can be formed, vide supra, from irradiation of $[Fe(CO)_4PPh_3]$. These data, taken together, imply that the alkene complexes of Ru are much more labile than the analogous complexes for Fe which themselves are thermally labile at 25 °C. Consistent with this conclusion, irradiation of $[Ru(CO)_4PPh_3]$ in 7.8 M 1-pentene in benzene while purging with N_2 to remove photoejected CO yields infrared spectral changes consistent with formation of $[Ru(CO)_3(PPh_3)(alkene)]$; two new bands in the CO stretching region were observed at 2033 and 1976 cm^{-1}. These two bands disappear rapidly upon exposing the solution to CO and starting material is regenerated.

Table III. Comparison of Photocatalyzed 1-Pentene Isomerization Using Various Iron and Ruthenium Catalyst Precursors

catalyst precursor	% conversn[b]	Φ[c]	t/c[d]
A. Mononuclear Iron Species[a]			
$Fe(CO)_5$	6.2	117	2.92
	11.9	112	2.93
$Fe(CO)_4P(OMe)_3$	3.6	79	1.46
	9.8	107	1.44
$Fe(CO)_4P(O\text{-}o\text{-tolyl})_3$	4.4	73	1.00
	11.6	76	1.15
$Fe(CO)_4PPh_3$	7.8	71	1.11
	12.7	58	1.20
B. Trinuclear Ruthenium Species[e]			
$Ru_3(CO)_{12}$	7.7	5.5	5.7
	13.8	5.0	6.2
$Ru_3(CO)_9(P(OMe)_3)_3$	6.5	1.6	5.7
	18.9	3.2	6.1
$Ru_3(CO)_9(P(O\text{-}o\text{-tolyl})_3)_3$	8.3	0.4	3.3
	16.7	0.6	3.4
$Ru_3(CO)_9(PPh_3)_3$	5.3	0.6	4.3
	10.0	0.9	3.4

[a] The catalysis solutions are neat 1-pentene containing 2×10^{-3} M iron carbonyl catalyst precursor. [b] % of 1-pentene isomerized to *trans*- and *cis*--2-pentenes. [c] Φ is the number of 1-pentene molecules isomerized per photon incident on the sample. Values are ±20%. [d] Ratio of *trans*-2-pentene to *cis*-2-pentene products. Values are ±5%. [e] The catalysis solutions are benzene solutions 1.76 M in 1-pentene and 10^{-3} M in ruthenium carbonyl catalyst precursor.

Effect of Variation in L on Photocatalyzed Isomerization of 1-Pentene. All the $[Fe(CO)_4L]$ and $[Ru_3(CO)_9L_3]$ (L = CO, PPh_3, $P(OMe)_3$, and $P(O\text{-}o\text{-tolyl})_3$) catalyst precursors effectively catalyze the isomerization of 1-pentene to *trans*- and *cis*-2-pentene upon near-UV, 355-nm, irradiation at 25 °C. The particulars of the 1-pentene isomerization are given in Table III. No isomerization occurs thermally at 25 °C on the same time scale as the photoreactions. All the catalyst precursors are capable of moving high concentrations of 1-pentene toward the thermodynamic ratio of linear pentenes,[19] demonstrating large turnover numbers (number of 1-pentene molecules consumed per metal atom initially present) which are at least 10^3. Further, observed initial quantum yields, Φ (number of 1-pentene molecules isomerized per incident photon), are high and often exceed unity, evidencing the photogeneration of a very active catalyst at room temperature.

The most important result is that the initial ratio of *trans*- to *cis*-2-pentene depends on the catalyst precursor used. There is a significant variation as the phosphorus ligand bonded to the iron carbonyl catalyst precursor is varied. The $[Fe(CO)_4L]$ catalyst precursors bearing sterically similar phosphorus ligands (PPh_3 and $P(O\text{-}o\text{-tolyl})_3$) give similar initial ratios of *trans*- to *cis*-2-pentene, whereas those bearing electronically similar phosphorus ligands ($P(OMe)_3$ and $P(O\text{-}o\text{-tolyl})_3$) do not yield similar ratios of 2-pentenes. The steric bulk of the phosphorus ligand affects the distribution of catalysis products; the bulkier the ligand the more *cis*-2-pentene formed relative to *trans*-2-pentene. Note that the ratio of *trans*- to *cis*-2-pentene obtained with $[Fe(CO)_5]$ is greater than those obtained with the phosphorus ligand substituted iron catalyst precursors. This is consistent with the steric bulk of the ligands affecting the catalysis product distributions,

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(18) (a) Tyler, D. R.; Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7888. (b) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C., private communication.

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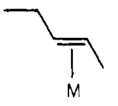
Table IV. Comparison of Photocatalyzed 1-Pentene and *cis*-2-Pentene Isomerization Using $Fe(CO)_5$ and $Fe(CO)_3(PPh_3)_2$ [a]

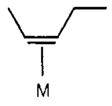
starting isomer	photocatalyst	extent conversn, %	Φ	(t/c)[b] or (t/1-pent)[c]
1-pentene, neat	$Fe(CO)_5$	6.2	117	2.92
		11.9	112	2.92
1-pentene, 5.0 M	$Fe(CO)_3(PPh_3)_2$	8.6	11.8	0.56
		11.2	7.7	0.57
		18.4	7.7	0.58
		43.2	2.7	0.65
cis-2-pentene, 0.0 M	$Fe(CO)_5$	4.9	71	13
		15.3	110	13
		25.9	75	14
		51.9	25	18
cis-2-pentene, 2.8 M	$Fe(CO)_3(PPh_3)_2$	2.8	1.3	3.7
		5.1	1.2	3.5
		10.5	1.2	3.2
		27.3	0.8	4.1
		38.4	0.6	5.9
		46.7	0.3	8.4

[a] All data from 2×10^{-3} M photocatalyst in hermetically sealed, degassed ampules. Irradiation source is 355 nm, ~2×10^{-6} einstein/min. [b] Ratio of *trans*- to *cis*-2-pentene starting with 1-pentene. [c] Ratio of *trans*- to 1-pentene starting with *cis*-2-pentene.

since CO, having an estimated cone angle of 95°,[3b] is less bulky than the phosphorus ligands studied here. Similar results are observed with the $[Ru_3(CO)_9L_3]$ catalyst precursors. Product distributions in thermal olefin isomerization reactions are sensitive to the steric interactions of the coordinated organic ligand with the other ligands present in the coordination sphere.[1b,4i,j] Bulky ligands favor the formation of the *cis*-olefin over the *trans*-olefin. Likewise, in these photocatalyzed 1-pentene isomerizations the bulky ligands favor the formation of *cis*-2-pentene relative to *trans*-2-pentene. This is reasonable since a *cis*-2-pentene ligand would be less sterically demanding than a *trans*-2-pentene ligand bonded to a metal, complexes A and B. Increasing the bulk of the other ligands in the coordination sphere could change the relative stability of A and B leading to thermodynamic effects that could result in a kinetic preference for formation of *cis*-alkenes. We conclude that the effect of the phosphorus ligand on the initial product distribution in these photocatalyzed reactions is primarily steric. The electronic properties may also be contributory, but the data suggest that electronic effects on the initial ratio of 2-pentenes are minor compared to the steric effects of the phosphorus ligands.



A

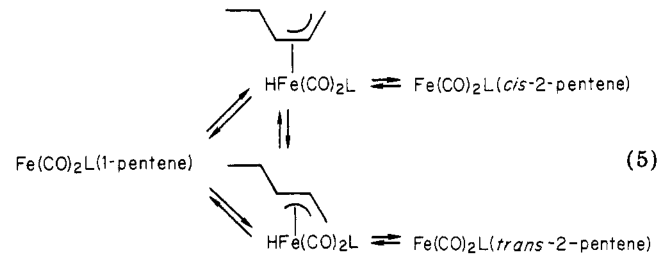


B

The consequences from electronic structure on geometrical structure is evident from the infrared spectra of the $[Fe(CO)_3L(1\text{-pentene})]$ complexes, vide supra and Table II. It is apparent from the data in Table III that L = $P(O\text{-}o\text{-tolyl})_3$ or PPh_3 do not give very different initial product ratios, despite the different structure for the 1-pentene complexes $[Fe(CO)_3L(1\text{-pentene})]$. However, it must be realized that $[Fe(CO)_3L(1\text{-pentene})]$ itself must be at least one step away from the active alkene isomerization catalyst. We believe that loss of a second CO (eq 4) must occur in order to actually effect catalysis. The

$$[Fe(CO)_3L(1\text{-pentene})] \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} [Fe(CO)_2L(1\text{-pentene})] + CO \quad (4)$$

resulting 16-valence electron species can reversibly form either a *syn*- or *anti*-π-allyl hydride as a precursor to the *cis*- and *trans*-2-pentene complexes, respectively (eq 5).



(5)

The point is that some species beyond the 18-valence electron $[Fe(CO)_3L(1\text{-pentene})]$ is where the ratio of initial products is determined. Thus, the different structures of $[Fe(CO)_3L(1\text{-pentene})]$ establish that the different P donors can give different geometries for the products, but the structure of these do not reveal the structure of the actual species that controls the initial distribution of olefin products.

In the catalysis experiments described so far, we began with 1-pentene and formed *trans*- and *cis*-2-pentene in a fashion such that the initial distribution of the two isomers was enriched in the thermodynamically less stable isomer, *cis*-2-pentene, compared to what the ratio would be at thermodynamic equilibrium. Ultimately, for all of the catalyst precursors the distribution of 1-pentene and *trans*- and *cis*-2-pentene does come to the thermodynamic equilibrium. But the kinetically controlled initial distribution of products can differ considerably from that at thermodynamic equilibrium. Indeed, irradiation of the complex $[Fe(CO)_3(PPh_3)_2]$ yields photocatalyzed 1-pentene isomerization giving an initial *trans*- to *cis*-2-pentene ratio of about 0.6, even lower than for $[Fe(CO)_4PPh_3]$. Thus, the greater steric bulk of the two PPh_3 ligands, compared to the single PPh_3, gives a larger kinetic preference for the less thermodynamically stable 2-pentene isomer. As illustrated by the data in Table IV, photocatalyzed isomerization of 1-pentene yields significant enrichment in the *cis*-2-pentene isomer, and quite interestingly the data show that in absolute terms at the greatest extent conversion there is more *cis*-2-pentene than would be present at the thermodynamic equilibrium of the linear pentenes which is ~3% 1-pentene, ~21% *cis*-2-pentene, and ~76% *trans*-2-pentene. Starting with pure *cis*-2-pentene further illustrates that the sterically demanding system, $[Fe(CO)_n(PPh_3)_2]$, yields the greater enrichment of the thermodynamically least stable product (Table IV). In fact, at 38.4% conversion the amount of 1-pentene present is

5.7% of all the linear pentene in the solution or roughly twice the amount present at the thermodynamic equilibrium. This clearly illustrates that the kinetically controlled product distribution from the photogenerated catalyst is enriched in the least stable isomer, but, as indicated above, the linear pentenes are ultimately equilibrated to the ratio that would be obtained from any other catalyst.

Quantum yields for isomerization generally exceed unity, indicating that a thermal catalyst is in fact generated. Moreover, the turnover rate of the catalyst must exceed the photoexcitation rate, $\sim 1.6 \times 10^{-6}$ einstein/min, otherwise the initial quantum yields would be less than one. But generally, we have used continuous irradiation to effect photocatalysis, since back reaction of coordinatively unsaturated species with photoejected CO precludes sustained catalysis at 25 °C after irradiation is terminated. The use of continuous irradiation raises the possibility that one could, in fact, drive the linear pentenes to a photostationary state that is enriched in 1-pentene, the least thermodynamically stable isomer. Empirically, this is not found; the ultimate distribution of the linear pentenes is just that found from conventional thermal catalysis.

To summarize our main finding then, we conclude that steric effects of ligands L in $[Fe(CO)_4L]$ or $[Ru_3(CO)_9L_3]$ promote the formation of the least thermodynamically stable pentene at initial stages of the photocatalyzed isomerization of pentene. Examples of other catalytic reactions in which the steric bulk of the phosphorus ligands affects the product distribution are the rhodium catalyzed hydroformylation reactions[4a,d,g,7] and some nickel-catalyzed olefin reaction.[4b,c] In the former system, Pruett and Smith[4a] showed that both the steric and electronic effects are important since increased electron donation from the ligand decreases the percentage of the normal isomer obtained but increased ligand bulk decreases the percentage of the normal isomer even more. In the nickel-catalyzed reaction of butadiene with morpholine Baker and coworkers[4b] showed that the percentage of products resulting from butadiene dimerization could be greatly enhanced by using bulky phosphorus ligands. The electronic effects of the phosphorus ligands on the product distribution were believed to be negligible in comparison. In both of these systems by knowing the nature of the effect of the phosphorus ligands on the product distribution, the reactions can be "tuned" to give the desired results simply by changing the phosphorus ligand. The results of our photocatalyzed 1-pentene isomerization reactions clearly demonstrate that the product distribution of photocatalyzed reactions can also be "tuned" in a similar manner, in this case by changing the steric bulk of the bonded phosphorus ligand. Inasmuch as the alkene isomerization that we have studied depends on the excitation rate (light intensity) it is clear that the activation energy for the catalysis is low. Future studies in this laboratory will include the use of photoexcitation to promote reaction where the temperature is sufficiently low to attempt to reach a situation where some step in the actual catalytic reaction is rate limiting.

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Registry No. 1-pentene, 109-67-1; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4P(OMe)_3$, 14878-71-8; $Fe(CO)_4P(O$-*o*-tolyl$)_3$, 18475-05-3; $Fe(CO)_4PPh_3$, 14649-69-5; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_9(P(OMe)_3)_3$, 38686-18-9; $Ru_3(CO)_9(P(O$-*o*-tolyl$)_3)_3$, 81522-95-4; $Ru_3(CO)_9(PPh_3)_3$, 15663-31-7; $Fe(CO)_4$(1-pentene), 58614-17-8; $Fe(CO)_4$(*cis*-2-pentene), 58476-94-1; $Fe(CO)_4$(*trans*-2-pentene), 58525-49-8; $Fe(CO)_3(PPh_3)_2$, 14741-34-5; $Fe(CO)_3(P(OMe)_3)_2$, 14949-85-0; $Fe(CO)_3(PPh_3)(P(OMe)_3)$, 81522-96-5; $Fe(CO)_3(PPh_3)(P(O$-*o*-tolyl$)_3)$, 81522-97-6; $Fe(CO)_3(PPh_3)$(1-pentene), 81522-98-7; $Fe(CO)_3(P(OMe)_3)$(1-pentene), 81522-99-8; $Fe(CO)_3(P(O$-*o*-tolyl$)_3)$(1-pentene), 81523-00-4; $Ru(CO)_3(PPh_3)$(1-pentene), 81523-01-5; $Ru(CO)_3(P(OMe)_3)_2$, 31541-94-3; $Ru(CO)_3(P(O$-*o*-tolyl$)_3)_2$, 81523-02-6; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Ru(CO)_4PPh_3$, 21192-23-4.

Syntheses, Spectral Properties, and Dynamic Solution Behavior of Bis(alkyne)bis(dithiocarbamato)molybdenum(II) Complexes

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Syntheses of a series of bis(alkyne)bis(dithiocarbamato)molybdenum(II) complexes with terminal, alkyl- and aryl-substituted alkynes are reported. Mixed bis(alkyne) complexes of the type $Mo(R^1C{\equiv}CR^2)(R^3C{\equiv}CR^4)(S_2CNR_2)_2$ have been prepared with $R^1 = R^2 = Ph$, $R^3 = Ph$, and $R^4 = H$, $R^1 = R^2 = Ph$, and $R^3 = R^4 = CO_2Me$, and $R^1 = R^2 = Et$, $R^3 = Ph$, and $R^4 = H$. Infrared spectroscopy has been used to probe the stretching frequency of the bound alkyne carbon–carbon multiple bond. The observed ^1H and ^{13}C chemical shift values of the acetylenic protons and carbons are compatible with previous empirical correlations relating alkyne donation from both filled π orbitals to these NMR observables. Dynamic NMR studies suggest that rotation of the bound alkyne ligands is common for these complexes with a barrier to rotation of 15.3 kcal mol^{-1} calculated for $Mo(EtC{\equiv}CEt)_2(S_2CNMe_2)_2$. Molecular orbital calculations based on the extended Hückel method provide insight into the destabilization of the vacant $d\pi$ LUMO of these complexes which results from alkyne $\pi_\perp$ donation and rationalizes the relative inertness of these formal 16-electron molybdenum(II) compounds.

Introduction

Studies of early transition metal alkyne complexes during the past few years have contributed to an emerging appreciation of the unique ability of alkyne ligands to utilize orthogonal metal $d\pi$ orbitals in order to serve simultaneously as both good single-faced π acceptors and good single-faced π donors.[1] The ligand-to-metal π-donor potential of the filled alkyne $\pi_\perp$ bonding component allows variable electron donor interactions which can formally

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