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Polymer-Bound Phosphine-Substituted Tetrairidium Carbonyl Clusters: Catalysts for Olefin Hydrogenation

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Unique tetrairidium carbonyl clusters were anchored to phosphine-functionalized poly(styrene-divinylbenzene), the metal species being identified by carbonyl infrared spectra as the clusters analogous to $[Ir_4(CO)_{21-x}(PPh_3)_x]$ (x = 1, 2, or 3). Infrared spectra of polymer membranes functioning as catalysts for ethylene and cyclohexene hydrogenation in a flow reactor at 1 atm and 40–80°C indicated that the predominant metal species in each catalyst was the originally prepared tetrairidium cluster. The catalysts were stable, exhibiting unchanged spectra and undiminished activity for as many as 5000 turnovers at temperature <90°C, but at temperatures >120°C, the iridium clusters aggregated to form crystallites. Catalytic kinetics measured at <90°C showed that for each olefin, the rate of hydrogenation decreased with an increasing number of phosphine substituents on the tetrairidium cluster. The results suggest that the metal clusters provided the catalytic sites, possibly formed by reversible cleavage of Ir–Ir or Ir–P bonds to generate coordinative unsaturation.

INTRODUCTION

The newly awakened interest in metal clusters as catalysts (*1*) is motivated by their apparent validity as models of metal surfaces and by the prospect of their offering new, selective catalysts for technologically important reactions like CO–H_2 conversions (*2*). But there are still only few examples of reactions for which it has been demonstrated that metal clusters (rather than mononuclear complexes and/or aggregates derived from clusers) provide the catalytic sites (*3*), and the literature reflects no attention to the practically important questions of stability of cluster catalysts and their separation from reaction products. We have addressed these questions, preparing unique tetrairidium clusters supported on solids, showing them to be active catalysts for ethylene hydrogenation and to be resistant to changes in structure and catalytic activity (*4*). We report here the first systematic study of supported clusters, describing procedures for synthesis of a series of polymer-anchored tetrairidium carbonyl clusters—having unique, systematically varied phosphine ligand environments—and characterization of their catalytic nature by infrared spectroscopy and by kinetics of ethylene and cyclohexene hydrogenation.

NOTATION

k	Rate constant, molecules/(Ir atom · sec · atm^{m+n})
m	Reaction order in olefin
n	Reaction order in hydrogen
P	Partial pressure, atm
r	Catalytic reaction rate, molecules/(Ir atom · sec)

EXPERIMENTAL METHODS

Syntheses. $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2, or 3) were prepared according to literature procedures (*5, 6*).

The monomers styrene, divinylbenzene (DVB), and *p*-bromostyrene were vacuum distilled to remove the polymerization inhibitors present in the commercially availa-

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ble reagents. The monomer *p*-styryldiphenylphosphine was synthesized according to a described procedure (*7*). Eleven-μm-thick polymer membranes were prepared from the monomers by Zundel's method (*8*).

Attachment of the clusters analogous to $[Ir_4(CO)_{12-x}(PPh_3)_x]$ ($x = 1$ or 2) on the polymer was performed according to a previously described procedure (*4*). To obtain [Ⓟ–$(PPh_2)_yIr_4(CO)_9(PPh_3)_{3-y}$] (where Ⓟ refers to poly(styrene-divinylbenzene), membranes incorporating clusters analogous to $[Ir_4(CO)_{10}(PPh_3)_2]$ were refluxed for 1 hr under N_2 in 300 ml of THF with triphenylphosphine (PPh_3/Ir_4 mol ratio = 1.5). The mixture was allowed to cool to room temperature, and the membranes were washed with THF, toluene, dichloromethane, and pentane and dried under vacuum at 25°C for 4 hr. If the reaction was carried out for as long as 6.5 hr, the metal was leached out of the membranes.

Measurement of kinetics of olefin hydrogenation. The polymer membranes incorporating tetrairidium clusters were tested as olefin hydrogenation catalysts in a flow reactor fed with ethylene or cyclohexene vapor, H_2, and He. The gas flow rates were individually measured with calibrated rotameters. H_2 and He flowed through a bed of supported copper, held at 300°C to remove traces of oxygen, and through a bed of zeolite 5A (Linde) to remove traces of water. Freshly distilled cyclohexene was introduced from a variable-speed syringe pump into a vaporizer made of a 0.1-m length of 6.4-mm stainless-steel tubing packed with glass beads. The vaporized reactant flowed out of the vaporizer with the hydrogen–helium mixture.

The reactant stream entered a flow reactor which was also an infrared cell, allowing monitoring of spectra of functioning catalysts (*9*). Prior to entering the reactor, the reactants flowed through reference cell, identical to the reactor but lacking the catalyst. Since the conversion in the reactor was always low, the absorptions due to the gases nearly cancelled, and the observed spectra were therefore indicative of the catalyst membrane in the functioning state.

The product gas stream, flowing steadily through a heated gas sampling valve, was sampled periodically and analyzed with a gas chromatograph. Ethylene and ethane were separated at 40°C on a 3-m × 3.2-mm stainless-steel column packed with Porasil C (80/100 mesh). Cyclohexene and cyclohexane were separated at 100°C on a 6-m × 3.2-mm stainless-steel column packed with Carbowax 20 M/2% KOH (80/100 mesh).

In a typical experiment, after the system had been flushed with He for 3 hr, H_2 and ethylene were introduced, and steady state was attained in approximately 7 hr. Subsequent changes in the partial pressures of the reactants required only about 30 min for establishment of a new steady state. Infrared spectra of the catalyst were recorded periodically during the kinetics experiments, but the infrared beam was usually off to prevent heating of the catalyst.

RESULTS

Polymer Synthesis

The $-PPh_2$ groups were incorporated in the phosphine-functionalized polymer membranes in two ways, giving widely different spacings of the groups. The first preparation involved the copolymerization of styrene, DVB, and *p*-styryldiphenylphosphine, giving block copolymers (*10*) with islands of high phosphine concentration in a sea of polymer. The second involved the nearly random copolymerization of styrene, DVC, and *p*-bromostyrene; the –Br groups in the polymer were partially replaced by $-PPh_2$ groups by reaction with lithium diphenylphosphide. Each of the phosphine-functionalized polymers was brought in contact with Zn, CO, and [$Ir(CO)_2Cl$(*p*-toluidine)] or $[Ir_2Cl_2(C_8H_{12})_2]$, and an *in situ* reaction resulted in polymers incorporating tetrairidium clusters coordinated to the $-PPh_2$ groups (*4*).

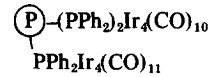
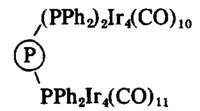
Attachment was attempted without success by contacting $[Ir_4(CO)_{12}]$ dissolved in toluene with polymers incorporating phosphine groups. The resulting polymers exhibited a broad infrared adsorption band in the carbonyl region, markedly different from the bands of the mono-, di-, or trisubstituted triphenylphosphine derivatives of $[Ir_4(CO)_{12}]$. This result indicates that more than one iridium species was attached to the polymer.

The membranes incorporating tetrairidium carbonyl clusters were identified by comparison of their carbonyl infrared spectra with those of the known molecular clusters. The spectra show that when the $-PPh_2$ groups in the polymer were randomly distributed and present in low concentration (i.e., with <2% of the benzene rings functionalized with $-PPh_2$ groups), the metal was almost uniquely present as [Ⓟ$-PPh_2Ir_4(CO)_{11}$] (Samples 1–4, Table 1; Fig. 1). When polymers with a higher phosphine concentration were used (those having >3% of the benzene rings functionalized with $-PPh_2$ groups), a mixture of clusters analogous to $[Ir_4(CO)_{11}PPh_3]$ and $[Ir_4(CO)_{10}(PPh_3)_2]$ was obtained (Sample 5, Table 1).

In contrast to these results, when the block copolymer incorporating $-PPh_2$ groups was used (having 8 to 15% of the

TABLE 1

Infrared Characterization of Polymer-Bound Tetrairidium Clusters and Their Molecular Analogs

Sample number	Sample	Solvent or phase	ν_{CO} (cm^{-1})
—	$[Ir_4(CO)_{11}PPh_3]$ (*5*)	CH_2Cl_2	2088 m, 2056 vs, 2020 s, 1887 vw, 1847 m, 1825 m
—	$[Ir_4(CO)_{10}(PPh_3)_2]$ (*5*)	CH_2Cl_2	2066 m, 2040 s, 2005 s, 1827 m, 1795 mb
—	$[Ir_4(CO)_9(PPh_3)_3]$ (*6*)	CS_2	2045 s, 1998 sb, 1991 sh, 1795 m, 1783 m
1, 2, 3, 4	Ⓟ$PPh_2Ir_4(CO)_{11}$	Membrane[a]	2087 m, 2054 vs, 2016 s, 1848 m
5	 Ⓟ$-(PPh_2)_2Ir_4(CO)_{10}$ $PPh_2Ir_4(CO)_{11}$	Beads[a] (*4*)	2090, 2054, 2016, 2068, 2044, 2006
6, 7	Ⓟ$-(PPh_2)_2Ir_4(CO)_{10}$	Membrane	2063 s, 2037 s, 2003 vs, 1827 m, 1797 m
8	 $(PPh_2)_2Ir_4(CO)_{10}$ Ⓟ $PPh_2Ir_4(CO)_{11}$	Membrane[a]	2089, 2055, 2014, 2069, 2044, 2007
9	Ⓟ$-(PPh_2)_yIr_4(CO)_9(PPh_3)_{3-y}$ $(y = 1,2)$	Membrane[a]	2087 vw, 2045 s, 1998 sb, 1990 sh

[a] Overlap of the bridging carbonyl bands with the bands of the polymer backbone prevented assignment of all the frequencies.

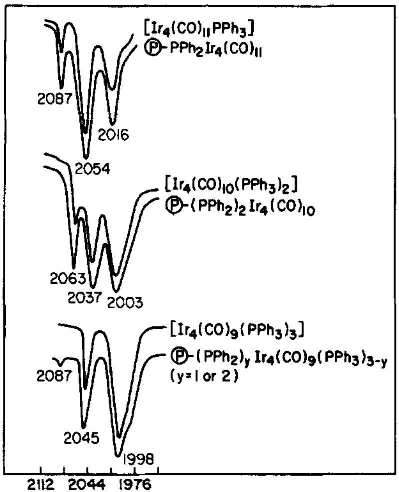


FIG. 1. Carbonyl infrared spectra of $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2, or 3) and their polymer-supported analogs.

benzene rings functionalized with $-PPh_2$ groups), species analogous to $[Ir_4(CO)_{10}(PPh_3)_2]$ were formed in the polymer (Samples 6 and 7, Table 1; Fig. 1). When <8% of the benzene rings in the polymer were functionalized with $-PPh_2$ groups, however, a mixture of species analogous to $[Ir_4(CO)_{11}PPh_3]$ and $[Ir_4(CO)_{10}(PPh_3)_2]$ was obtained (Sample 8, Table 1).

Attempts to prepare [Ⓟ$-(PPh_2)_3Ir_4(CO)_9$] by variation of the synthesis conditions were not successful, but polymers presenting carbonyl infrared spectra like that of $[Ir_4(CO)_9(PPh_3)_3]$ were prepared by reacting PPh_3 in THF with [Ⓟ$-(PPh_2)_2Ir_4(CO)_{10}$]. Since the number of ligands exchanged with PPh_3 in this synthesis was not determined, this product is designated as [Ⓟ$-(PPh_2)_yIr_4(CO)_9(PPh_3)_{3-y}$], where y = 1 or 2 (Sample 9, Table 1).

The important results of the syntheses are that polymers incorporating nearly unique tetrairidium cluster species having 1, 2, or 3 phosphine substituents were prepared, with purities estimated from the spectra to be >95%. The analyses of these samples (performed by Schwarzkopf Microanalytical Laboratory, New York, N.Y.) are summarized in Table 2.

Catalytic Kinetics

The polymers incorporating tetrairidium clusters were catalytically active, H_2 and the olefin giving the corresponding paraffin as the only observed product. The negligibility of intramembrane diffusion resistance was demonstrated by results showing that a 25-μm-thick membrane had the same catalytic activity per Ir atom as the standard 11-μm-thick membrane. Details given elsewhere (*11*) demonstrate the negligibility of other transport effects. The data therefore provide a measure of the intrinsic catalytic activity of each polymer. The numbers of turnovers (molecules of olefin converted per Ir atom) experienced by the polymers ranged from 250 to 5000, demonstrating that the reactions were indeed catalytic.

Kinetics data for the catalytic reactions were obtained over the following ranges of partial pressures: $0.2 \leq P_{H_2} \leq 0.9$; $0.2 \leq P_{\text{olefin}} \leq 0.9$ atm. Helium was used as a diluent to allow variation of the partial pressure of one reactant as the partial pressure of the other was held constant. Total pressure varied from 1.00 to 1.10 atm.

TABLE 2

Analysis of the Polymers Incorporating Tetrairidium Clusters[a]

Sample number	Elemental analysis, wt%		P/Ir_4 mol ratio
	P	Ir	
1	0.11	0.60	4.5
2	0.15	0.26	14.3
3	0.32	0.25	31.7
4	0.28	1.82	3.8
5	1.28	11.10	2.86
6	2.08	7.42	6.9
7	1.51	10.89	3.4
8	1.50	9.51	3.9
9	1.88	6.99	6.6

[a] The polymers were crosslinked with 2 mol% DVB.

The hydrogenation kinetics for each olefin was well represented by

$$r = k\, P_{\mathrm{olefin}}^{m}\, P_{\mathrm{H_2}}^{n}. \qquad (1)$$

The values of k, m, and n giving the best fits of the data were determined by a standard nonlinear least-squares regression technique (*12*). The kinetics results are summarized in Table 3, with typical data shown in Fig. 2.

All three polymers, [Ⓟ-$PPh_2Ir_4(CO)_{11}$], [Ⓟ-$(PPh_2)_2Ir_4(CO)_{10}$], and [Ⓟ-$(PPh_2)_yIr_4(CO)_9(PPh_3)_{3-y}$] ($y$ = 1 or 2) were found to be active, stable catalysts for ethylene hydrogenation. The polymers [Ⓟ-$PPh_2Ir_4(CO)_{11}$] and [Ⓟ-$(PPh_2)_2Ir_4(CO)_{10}$] catalyzed cyclohexene hydrogenation. The activity of the former (Sample 3) was too low to allow measurement of the kinetics, but the rate of reaction at 80°C (with $P_{C_6H_{10}}$ = 0.2 atm and P_{H_2} = 0.8 atm) was about 0.001 molecules/Ir atom · sec. The kinetics observed with the latter catalyst (Sample 6) is reported in Table 3. The polymer [Ⓟ-$(PPh_2)_yIr_4(CO)_9(PPh_3)_{c-y}$] ($y$ = 1 or 2) (Sample 9) had a low activity for cyclohexene hydrogenation, the observed rates at 81°C being $<10^{-5}$ molecules/Ir atom · sec.

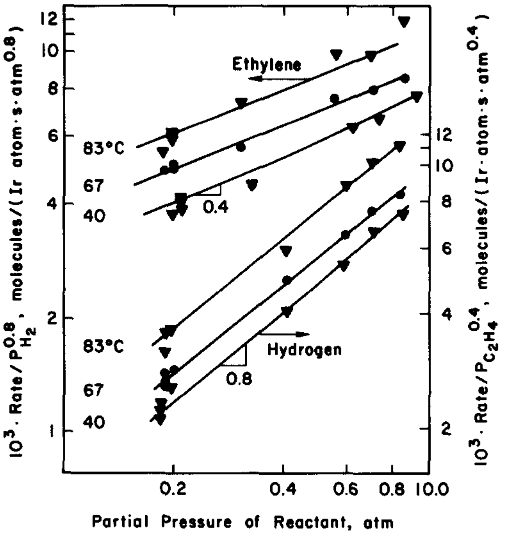


FIG. 2. Kinetics of ethylene hydrogenation catalyzed by Ⓟ-$(PPh_2)_2Ir_4(CO)_{10}$ (Sample 6) at 1 atm.

For each catalyst, the activity for ethylene hydrogenation was about 10 times greater than that for cyclohexene hydrogenation. Even traces of CO in the reactant stream inhibited the reactions so strongly

TABLE 3

Kinetics of Olefin Hydrogenation Catalyzed by Polymers Incorporating Clusters Analogous to $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2, or 3)

$r = kP_{\mathrm{olefin}}P^{n}_{H_2}$

Olefin	x	Sample number	T (°C)	k[a] (molecules/ Ir atom · sec · atm^{m+n})	m	n
Ethylene	1	1	40	0.079 ± 0.01	0.69 ± 0.08	0.96 ± 0.08
Ethylene	1	1	53	0.090 ± 0.01	0.63 ± 0.12	0.96 ± 0.12
Ethylene	1	1	64	0.108 ± 0.02	0.63 ± 0.09	1.01 ± 0.096
Ethylene	1	2	40	0.081 ± 0.01	0.56 ± 0.06	1.03 ± 0.06
Ethylene	2	6	40	0.0080 ± 0.0006	0.40 ± 0.04	0.80 ± 0.04
Ethylene	2	6	67	0.0094 ± 0.001	0.39 ± 0.06	0.74 ± 0.06
Ethylene	2	6	83	0.0128 ± 0.001	0.46 ± 0.06	0.78 ± 0.06
Ethylene	2	7	40	0.0069 ± 0.0008	0.30 ± 0.05	0.90 ± 0.05
Ethylene	3	9	70	0.006 ± 0.0002	0.87 ± 0.15	0.55 ± 0.14
Cyclohexene	2	6	81	0.0064 ± 0.002	1.51 ± 0.2	0.62 ± 0.17

[a] In calculating activation energies for ethylene hydrogenation, the reaction orders in olefin and hydrogen were assumed to be 2/3 and 1.0, respectively, for x = 1, and 0.4 and 0.8, respectivley for x = 2. The rate constants at the several temperatures were then reevaluated and fitted to the Arrhenius equation. The activation energies were 2.5 ± 0.3 kcal/mol for x = 1 and 2.2 ± 0.6 kcal/mol for x = 2.

that no conversion could be observed, but when the reactor was purged with reactants free of CO, the original catalytic activity was regained. For both reactions, the rate decreased with increasing phosphine substitution on the cluster (Fig. 3). Experiments performed with varying phosphine/Ir_4 ratios in the polymer (with some of the $-PPh_2$ groups being uncoordinated) showed that the rate of ethylene hydrogenation was nearly independent of the concentration of uncoordinated $-PPh_2$ groups (Table 4).[3]

During all the flow-reactor experiments, the catalysts exhibited unchanged activity, provided that the temperature did not exceed 90°C. The infrared spectra also remained unchanged, being indistinguishable from those of the originally prepared catalysts under all reaction conditions, provided that temperatures were <90°C.

When the polymers were heated to 120°C, however, they were unstable, and the carbonyl bands merged in a period of about 1 hr into a broad band located at 2050 cm^{-1}. This band is indicative of CO bonded to aggregated iridium species (*4*, *13*). The darkening of the samples confirmed the aggregation of the metal.

DISCUSSION

The importance of the synthetic routes described here is that they open up the possibility of systematic investigations of

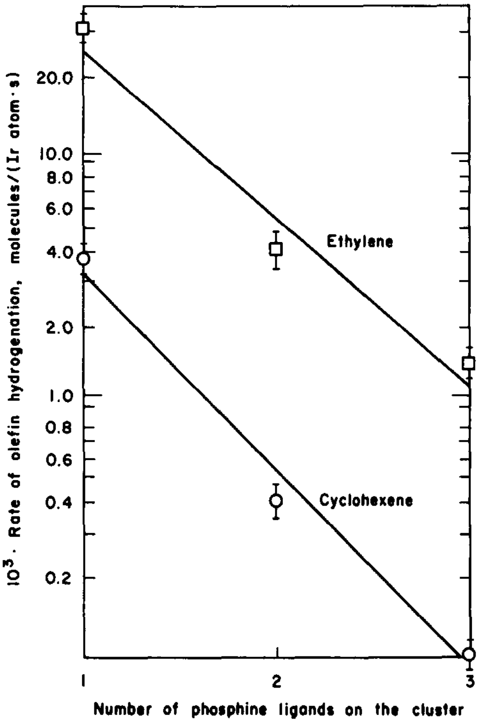


FIG. 3. Effect of the ligand substitution on the rate of hydrogenation of: □ ethylene, P_{H_2} = 0.8 atm, $P_{C_2H_4}$ = 0.2 atm, T = 70°C; ○ cyclohexene, P_{H_2} = 0.72 atm, $P_{C_6H_{10}}$ = 0.15 atm, T = 80°C.

the catalytic nature of supported polynuclear metal species having unique, well-defined structures.[4] The spectra of the functioning catalysts indicate that tetrairidium clusters with unique ligand environments were the predominant metal species in each catalyst, but it remains to be determined whether the central premise of the work—namely, that the metal clusters themselves provided the catalytic sites—has been met.

The reaction orders given in Table 3 are different from those expected for catalytic hydrogenation on metal surfaces. Typical reaction orders for olefin hydrogenation catalyzed by metal surfaces are 1 in hyrogen and 0 in olefin (*17*). The kinetics results therefore suggest that the catalytic groups

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[3] Attachment was also attempted by contacting the polymer support incorporating $-PPh_2$ groups and $-Br$ groups with $[Ir_4(CO)_{11}PPh_3]$ dissolved in benzene. It was thought that the attachment with $[Ir_4(CO)_{11}PPh_3]$ might produce polymer-anchored disubstituted tetrairidium clusters by ligand exchange, which was expected to be easier with $[Ir_4(CO)_{11}PPh_3]$ than with $[Ir_4(CO)_{12}]$, because of the activation of the cluster by the $-PPh_3$ ligand. This synthesis would have allowed a comparison of the rate of olefin hydrogenation catalyzed by [Ⓟ–$(PPh_2)_2Ir_4(CO)_{10}$] in a block copolymer and that catalyzed by the same cluster in a random copolymer. The synthesis was not successful, however, giving no attached species at room temperature and giving a complex mixture of attached species after 10 min of refluxing in benzene.

[4] In related work, polymer-supported tetraruthenium clusters (*14*), polymer-supported bimetallic clusters (*15*), and (phosphine-functionalized) silica-supported tetrairidium clusters (*16*) have been prepared and studied as olefin hydrogenation catalysts.

were not small amounts of metal crystallites which might have been present in undetectibly low concentrations. The reproducibility of the results and the strong dependence of the catalytic activity on the ligand environment of the cluster (Fig. 3) also suggest that the clusters themselves provided the catalytic sites.

The intriguing question that remains is why does the catalytic activity decrease with increasing phosphine substitution on the tetrairidium clusters? The electron-donating effect of the phosphine groups might suggest the opposite effect (*18*), but the possibility of dominant steric effects remains (*19*). The literature (*20*) indicates that steric effects associated with phosphine ligands often are at least as important as electronic effects in homogeneous catalysis.

To summarize, the kinetics and the infrared spectra—indicating the presence of tetrairidium clusters as the only metal species in the catalysts—are consistent with the hypothesis that the attached clusters themselves were involved in the catalytic cycles for olefin hydrogenation. With this working hypothesis, we proceed to suggest mechanisms that might provide catalytic sites on the clusters. Presuming that sites having incomplete coordination are necessary for bonding of the reactants (which is consistent with the observed inhibition of reaction by CO), we infer that the generation of sites can most easily be accounted for by reversible dissociation of Ir–CO bonds, of Ir–P bonds, or of Ir–Ir bonds.

If the first suggestion were correct, then the CO concentration recorded by infrared spectroscopy should have decreased because the continuous stream of reactants in the flow system would have flushed out the displaced CO. Since no change in the carbonyl spectra of the functioning catalysts was observed with catalysts experiencing thousands of turnovers, we infer that the Ir–CO bond dissociation is a very unlikely possibility for the formation of an active site on the cluster.

TABLE 4

Lack of Influence of the P/Ir_4 Ratio on the Rate of Ethylene Hydrogenation[a]

Sample number	Catalyst	P/Ir_4 mol ratio	Rate (molecules/ Ir atom · sec)
1	[Ⓟ-$PPh_2Ir_4(CO)_{11}$]	4.5	2.13×10^{-2}
2	[Ⓟ-$PPh_2Ir_4(CO)_{11}$]	14.3	2.53×10^{-2}
6	[Ⓟ-$(PPh_2)_2Ir_4(CO)_{10}$]	6.9	3.60×10^{-3}
7	[Ⓟ-$(PPh_2)_2Ir_4(CO)_{10}$]	3.4	3.76×10^{-3}

[a] $P_{C_2H_4} = 0.2$ atm, $P_{H_2} = 0.8$ atm, $T = 40°C$, $P = 1$ atm.

The other two possibilities are difficult to distinguish, there being too few thermodynamics data in the literature to form a basis for a good estimate of the Ir–Ir and Ir–P bond strengths (*1*). One might suppose, however, that if coordinative unsaturation resulted from Ir–P bond breaking, then excess $-PPh_2$ groups in the flexible polymer matrix might act as reaction inhibitors; the data of Table 4 show that they do not. But the literature provides many examples of the importance of metal–P bond cleavage in mononuclear species (*21*), and examples of metal–metal bond breaking have also been suggested for the generation of catlaytic sites (*22*). Both mechanisms are therefore considered plausible.

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REFERENCES

1. Muetterties, E. L., *Bull. Soc. Chim. Belg.* **84,** 959 (1975); **85,** 451 (1975). Muetterties, E. L., Rhodin, T. N., Band, E., Brucker, C. F., and Pretzer, W. R., *Chem. Rev.* **79,** 91 (1979).
2. Pruett, R. L., *Ann. NY Acad. Sci.* **295,** 239 (1977).
3. Deeming, A. J., and Hasso, S., *J. Organometal. Chem.* **114,** 313 (1976); Keister, J. B., and Shapley, J. R., *J. Amer. Chem. Soc.* **98,** 1056 (1976).
4. Rafalko, J. J., Lieto, J., Gates, B. C., and Schrader, G. L., Jr., *J. C. S. Chem. Comm.* 540 (1978);

Lieto, J., Rafalko, J. J., Minkiewicz, J. V., Rafalko, P. W., and Gates, B. C., *in* "Fundamental Research in Homogeneous Catalysis," Vol. 3, M. Tsutsui, ed. Plenum, New York, 1979.

5. Stuntz, G. F., and Shapley, J. R., *Inorg. Chem.* **15,** 1493 (1976).
6. Malatesta, J., and Caglio, G., *J. C. S. Chem. Comm.* 420 (1976).
7. Rabinowitz, R., and Marcus, R., *J. Org. Chem.* **26,** 4157 (1961).
8. Zundel, G., *in* "Hydration and Intermolecular Interaction. Infrared Investigations with Polyelectrolyte Membranes." Academic Press, New York, 1969.
9. Jarrell, M. S., and Gates, B. C., *J. Catal.* **40,** 225 (1975).
10. Rabinowtiz, R., Marcus, R., and Pellon, J., *J. Polym. Sci.* **A2,** 1241 (1964).
11. Lieto, J., Ph.D. thesis, University of Delaware, 1979.
12. Marquardt, D. W., *J. Soc. Ind. Appl. Math.* **11,** 431 (1963).
13. Howe, R. F., *J. Catal.* **50,** 196 (1977).
14. Otero-Schipper, Z., Lieto, J., and Gates, B. C., *J. Catal.*, in press.
15. Pierantozzi, R., McQuade, K. J., Gates, B. C., Wolf, M., Knözinger, H., and Ruhmann, W., *J. Amer. Chem. Soc.* **101,** 5436 (1979).
16. Studer, D. D., M.Ch.E. thesis, University of Delaware, 1979; Studer, D. D., and Schrader, G. L., Jr., unpublished results.
17. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
18. Chini, P., Martinengo, S., and Garlaschelli, G., *J. C. S. Chem. Comm.* 709 (1972).
19. Vaglio, G. A., and Valle, M., *Inorg. Chim. Acta* **30,** 161 (1978).
20. Tolman, C. A., *Chem. Rev.* **77,** 313 (1977).
21. Bingham, D., Webster, D. E., and Wells, P. B., *J. C. S. Dalton,* 1928 (1972); 1514 (1974).
22. Johnson, B. F. G., Lewis, J., and Pippard, D., *J. Organometal. Chem.* **160,** 263 (1978); Bar, G., Dietler, V. K., Pino, P., and Pöe, A., *J. Organometal. Chem.* **154,** 301 (1978).