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Design of Novel Catalysis Based on Olefins

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3) Executive Summary

Kazakhstan is rich in phosphates, oil and, in particular, coal. It is also the world's largest producer of phosphorous. The purpose of this project is to develop coal-based organic synthesis. Since olefins can be produced from coal by Fischer-Tropsch technology in high yields, our aim is to develop novel catalytic reactions involving olefins. Particularly desirable are selective additions of small molecules, such as water, ammonia, CO_2 and phosphine, to olefins. Phosphine is abundant in Kazakhstan because of its large phosphorous industry. Our approach involves rational catalytic design based on mechanistic understanding of the modes in which a transition metal can activate the desirable substrates. In this project, work at the Weizmann Institute of Science has provided a comprehensive picture of the scope and mechanism of the activation of water and alcohols by transition metal (particularly iridium) complexes and the mechanism of catalytic activation of olefins involving insertion in Pd-C bonds. New metal complexes were prepared. In Kazakhstan, new homogeneous catalytic reactions of PH3 and olefins and a heterogeneous catalytic process for the addition of CO_2 to olefins, utilizing supported metal catalysts have been developed. Initial results showing catalysis of water addition to propylene to give n-propanol promoted by bimetallic heterogeneous catalysts at high temperature have been obtained in Kazakhstan. The synergism between rational catalytic design based on the mechanistic understanding, developed at the Weizmann Institute, and catalysis discovered in Kazakhstan proved to be fruitful.

Mutual visits of the principal investigators in Kazakhstan and the Weizmann Institute had taken place, and two senior scientists from Kazakhstan were trained at the Weizmann Institute for 4 months. Prof. Dorfman spent two weeks at the Weizmann Institute for the purpose of joint research using electrochemicl cells developed in Kazakhstan. A glass pressure reactor developed at the Weizmann Institute was given to Kazakhstan. Laboratory supplies and chemicals were purchased by Weizmann Institute and shipped to Kazakhstan.

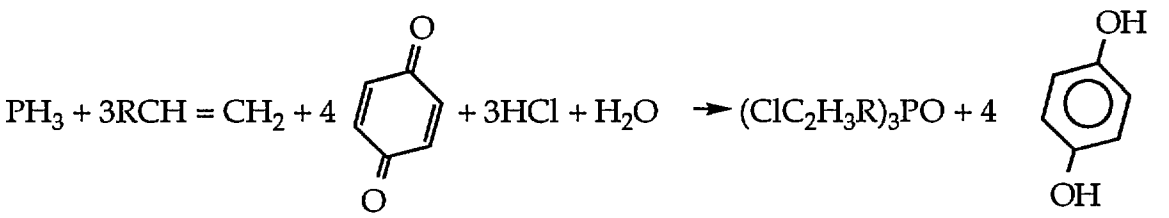
4) Research Objectives

The overall aim of the project is to develop novel catalytic reactions based on olefins and other coal-derived products. Towards this end, more specific goals are mechanistic understanding of water and ammonia activation by transition metals; mechanistic understanding of olefin insertion into M–R bonds (R=C, H, N, O); the development and study of catalytic reactions based on these fundamental processes, and the development of effective heterogeneous catalysis based on olefins and small molecules (phosphine, CO_2, etc.).

5) Methods and Results

A. Oxidative alkylation of PH_3 by terminal olefins and benzoquinone catalyzed by Pd(II), Hg(II) and Ag(I).

Kazakhstan is one of the largest phosphorous producers in the world. In this industry, much PH_3 is formed as a by-product and routes for its utilization are being sought. Dorfman's group discovered a new reaction involving PH_3 – its oxidative addition to terminal alkenes:



The terminal olefins $RCH{=}CH_2$ (R = Ph, Bu, C_6H_{13}) readily react at 50-80°C with PH_3, even at low phosphine partial pressure in gas mixtures (<4 10^3 Pa), in dioxane solutions of MCl_2 (M = Hg, Pd) and $C_6H_4O_2$ to give tris(β-chlor-α-alkyl) phosphine oxide $(ClC_2H_3R)_3PO$ [or tris(β-chlor-α-phenylethyl) phosphine oxide $(ClC_2H_3R)_3PO$ in the case of styrene].

Apart from the main reaction of PH_3 oxidative alkylation by olefin, the side reaction of PH_3 arylation by $C_6H_4O_2$, yielding tetra(dihydroxyphenyl)-phosphonium chloride $[C_6H_3(OH)O_2]_4PCl$, takes place. The rise of H_2O, HCl, LiCl, CH_3CN and Py concentrations and the exchange of styrene to 1-octene or 1-hexene lead to an increase in the phosphonium salt and a decrease in the phosphine oxide yield. Bis(hydroxyphenyl)phosphite $[C_6H_4(OH)O]_2HPO$

appeared in the products at [H_2O] >10%.

The kinetics, mechanism and products fo the main and side reactions were studied with a number of techniques and methods: redox potentiometry, ^{31}P NMR spectroscopy, gas chromatography, inhibition of radicals, chemical modeling, orbital symmetry. The optimal conditions of a new reaction were found.

Full details of these interesting reactions are given in the appendixes.

B. Reactions of CO_2 with olefins

The reaction between CO_2 and 1-hexane was investigated by Prof. Zakumbaeva in Kazakhstan. A continuous flow pressure reactor was used and various pressures and temperatures were applied. The best catalyst was found to be Ru/Co (1:1) supported on Al_2O_3. Quantum mechanical calculations were carried out in order to determine the mechanism of CO_2 intereaction with the catalyst. A detailed description of these studies appears in the appendix.

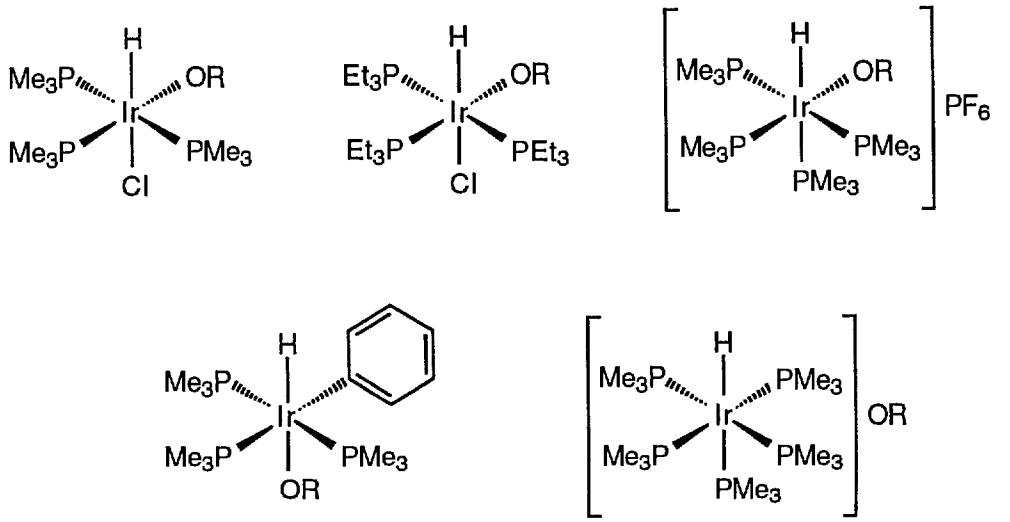
C. Olefin insertion into Pd-C bonds

The synthetically useful Pd catalyzed reactions of aryl chlorides with olefins involves, as a crucial step, the insertion of olefin into Pd–C bonds. This reaction is very sensitive to the chelating ligand bound to palladium. The olefin insertion into Pd–Ar (Ar = aryl) has been studied in detail and the role of the chelating ligand has been clarified. This study has been published and a reprint is attached.

D. O-H activation

a. Oxidative Addition of Water and Alcohols to Late Transition Metals. Synthesis and Mechanism.

In this research we used mechanistic analysis in order to gain deep understanding of the factors dominating the O-H oxidative addition by late transition metals, and of the transformations taking place within the coordination sphere of the adducts. A synthetic method to stable hydrido-hydroxo and -alkoxo complexes of the late transition metals was developed, using direct oxidative addition of the O-H bond to electron rich complexes at low temperature, in the least polar media possible. The families of H-Ir-OR complexes generated by this method in this study are depicted below.



Due to the kinetic and thermodynamic instability of the few H-M-OR generated prior to this work, the mechanism of this reaction was never studied systematically. We examined in detail the O-H cleavage by five electron rich d^8 iridium complexes. In light of the current knowledge about oxidative addition reactions, the differences between these complexes seemed small. However, we have demonstrated in this work that the mechanism of the O-H bond oxidative addition is strongly dependent on the ligand environment of the reactive complex. Four (!) different mechanisms were observed in solution (an additional one prevails in the gas phase).

Oxidative addition of water and aliphatic alcohols to $IrCl(PMe_3)_3$ (**1a**) in benzene yielded the *cis*-hydrido-hydroxo or -alkoxo product *mer-cis*-$HIr(OR)Cl(PMe_3)_3$ (R = H, Me, Et, 1-pentyl, 2-propyl). The reaction rate depended on the nature of the alcohol (methanol > 1-pentanol >> 2-propanol). The oxidative addition was retarded by coordinating solvents but was accelerated in protic media. The reaction rate was not influenced by the presence of either catalytic amounts of strong acids or of excess of LiCl. The analogous methanol addition to $IrCl(PEt_3)_3$ (**9**) was independent of the concentration of PEt_3. The activation parameters for the oxidative addition of methanol to **1a** are: $\Delta H^{\ddagger}_{obs}$ = 8.7(7) kcal mol^{-1}; $\Delta S^{\ddagger}_{obs}$ = -37.6(56) e.u.; $\Delta G^{\ddagger}_{obs}$ (298) = 19.9(32) kcal mol^{-1}. The primary kinetic isotope effect obtained for the oxidative addition is k_{CH_3OH}/k_{CH_3OD} = 2.00(20). The secondary kinetic effect of each β-deuterium in methanol can be estimated to be 1.17. Anionic ligand redistribution competed with the oxidative addition reaction, generating $Ir(OCH_3)(PMe_3)_3$, *mer-cis*-$HIr(OCH_3)_2(PMe_3)_3$ and

mer-cis-$HIrCl_2(PMe_3)_3$.

The data indicates that O-H oxidative addition to **1a** proceeds by an S_N2-like mechanism, in complete analogy to the much studied oxidative addition of alkyl halides. 16e **1a** itself is the reactive nucleophile. It is due to this fact that cleavage of weaker C-H bonds in methanol is not competitive to that of the O-H bond, since C-H bonds were reported to oxidatively add to 14e species. Alcohol coordination to the metal is not on the reaction coordinate, and the O-H bond is not cleaved prior to formation of the Ir-H bond. Based on steric arguments we concluded that the transition state is bent (three-centered but asymmetric), and not linear, thus shedding light on the shape of the polarized transition state during oxidative additions of polarized bonds.

The *mer-cis*-$HIr(OR)Cl(PR'_3)_3$ (R = H, Me; R' = Me, Et) products undergo the reverse reductive elimination of O-H bonds, enabling for the first time direct study of this type of reactivity. Fast equilibrium between *mer-cis*-$HIr(OCH_3)Cl(PEt_3)_3$ (**10**) and $IrCl(PEt_3)_3$ + CH_3OH was obtained in a C_6D_6 solution containing excess methanol with $\Delta H° = 20.7(14)$ kcal mol^{-1} and $\Delta S° = 67(4)$ e.u. From this equilibrium, it is possible to estimate $D(Ir\text{-}OCH_3)$ as 61-68 kcal mol^{-1}, much stronger than previously guessed. The concomitant irreversible β-H elimination from **10** was found too slow to prevent the system from reaching equilibrium. For the analogous PMe_3 complex, the equilibrium constant is strongly shifted towards *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (**2**). Kinetic measurements in a CD_3OD/C_6D_6 solution showed that the exchange of Ir-H to Ir-D in **2**, for which the O-H reductive elimination is rate determining, is 3.7 times faster than the competing β-H elimination process. The data suggests, that contrary to previous expectations, formation of alcohols by O-H reductive elimination can compete *favorably* with β-H elimination.

NMR follow-up of the water oxidative addition to $[Ir(PMe_3)_4]PF_6$ (**14**) revealed that both *trans* (**28**) and *cis* (**15**) $[HIr(OH)(PMe_3)_4]PF_6$ were initially formed. Yet, the *cis* adduct **15** was the only final product. Unlike the O-H oxidative additions to $IrCl(PR'_3)_3$ (**1** and **9**), **15** was irreversibly formed. A good fit to the kinetic results was possible only with a mechanistic model, in which the *trans* and the *cis* O-H cleavage products are formed by competing reactions. Both oxidative additions are first order in **14** and in the water concentration. The activation parameters derived for the *trans* oxidative addition process are: $\Delta H^{\ddagger}_{obs}$ = 9.2 kcal mol^{-1}; $\Delta S^{\ddagger}_{obs}$ = -54 e.u.; $\Delta G^{\ddagger}_{obs}$ (298) = 25.4 kcal mol^{-1}. This reaction is

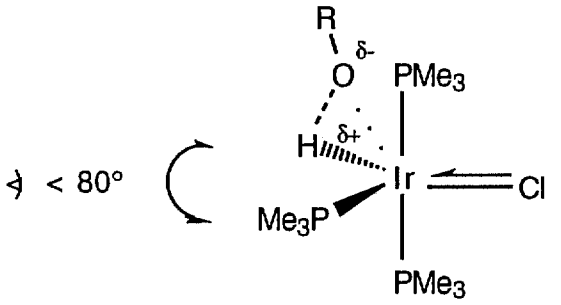
slightly endothermic, with $\Delta H° = -14.7$ kcal mol^{-1}; $\Delta S° = -51$ e.u.; $\Delta G°$ (298) = 0.41 kcal mol^{-1}. The activation parameters derived for the *cis* oxidative addition process are: $\Delta H^{\ddagger}_{obs} = 13.9$ kcal mol^{-1}; $\Delta S^{\ddagger}_{obs} = -40$ e.u.; $\Delta G^{\ddagger}_{obs}$ (298) = 25.8 kcal mol^{-1}. The kinetic isotope effect obtained for the oxidative addition is $k_{H2O}/k_{D2O} = 7.8$. The analogous reaction with methanol also ended with the *cis* addition product *cis*-[HIr(OCH$_3$)(PMe$_3$)$_4$]PF$_6$ (**17**). Yet, *cis*-[H$_2$Ir(PMe$_3$)$_4$]PF$_6$ (**18**) was formed concomitantly. As we found that **17** is stable against β-hydride elimination under the conditions employed for the oxidative addition reaction, it is clear that **18** could be obtained only from an unsaturated intermediate en-route from **14** to **17**. The reactions of water and methanol with **14** were much slower than with IrCl(PMe$_3$)$_3$ (**1a**) and IrCl(PEt$_3$)$_3$ (**9**).

The data indicates that the faster reaction, yielding the *trans* hydrido hydroxo product **28**, proceeds by protonation on the metal, and is reversible. The *cis* hydrido hydroxo adduct **15** is irreversibly formed by the slower process that follows the steps: (a) phosphine dissociation and coordination of a water molecule; (b) slippage of the coordinated water to generate an η^2-(H-OH) intermediate; (c) cleavage of the O-H bond, probably by the same mechanism that prevails in the oxidative addition of H-H and C-H bonds; (d) phosphine reassociation that can lead either to the *trans* adduct **28** or irreversibly to the *cis* **15**.

It was surprising to find that *mer-cis*-HIr(OCH$_3$)Cl(PMe$_3$)$_3$ (**2**) undergoes facile O-H reductive elimination, while the more sterically hindered and less electron rich **15** is stabilized against it. A plausible explanation to this observation is that *the π-donating chloride can stabilize the unsaturated transition state common to the O-H oxidative addition to **1a** and to the reverse reductive elimination from **2** and mer-cis-HIr(OH)Cl(PMe$_3$)$_3$ (**6**), thus accelerating both.* As [Ir(PMe$_3$)$_4$]PF$_6$ (**14**) has no π-donor, the transition state for its water oxidative addition (and for the reverse reductive elimination) by the S_N2-like mechanism is not stabilized, and eventually a different reactivity pathways are chosen.

π-donor stabilization of an oxidative addition transition state was not suggested before. However, the structure of unsaturated d^6 iridium complexes stabilized by a single π-donor was previously studied by X-ray crystallography, and analyzed by theoretical calculations. Applying the principles emerging from these studies to the transition state of the O-H oxidative addition, we suggest its

geometry resemble the drawing below. Based on this structure, *we are able to predict the stereochemical course of polarized bonds oxidative addition to d^8 complexes having a single π-donor.*



To support our idea of π-donor acceleration of the oxidative addition of polarized bonds, we examined the reaction of $(C_6H_5)Ir(PMe_3)_3$ (**19**) with water and methanol. **19** is more electron rich than **1a** (while cationic **14** is less basic). Likewise, **19** is sterically similar to **1a**, while **14** is more hindered than both. Hence, the mechanism of O-H oxidative addition by **19** were expected to resemble that of **1a**, unless the π-donor ligand is important in determining the oxidative addition mechanism. Only in that case could we predict a mechanism similar to that of **14**.

The reaction of **19** and methanol yielded the *trans* oxidative addition product. Unusually, $\Delta H^{\ddagger}_{obs}$ obtained is negative (-10.6(4.6) kcal mol^{-1}). A negative $\Delta H^{\ddagger}_{obs}$ can be obtained only if the studied reaction proceeds through an intermediate. $\Delta S^{\ddagger}_{obs}$ is also unusual in its magnitude (-102.5(165) e.u.). Nevertheless, $\Delta G^{\ddagger}_{obs}$ (298) is within the expected range (19.9(5) kcal mol^{-1}). We have also determined the kinetic isotope effect k_{CH_3OH}/k_{CD_3OD} = 6.6(5). With this information, we ruled out the S_N2-like mechanism for the O-H activation by **19**, thus showing that **19** and **1a** behave differently. Our data indicates a complex mechanism for this process involving protonation of the metal, that is a variation of the reactivity of **14**. It therefore supports our suggestion that π-donation from an ancillary ligand is of paramount importance in determining the O-H cleavage mechanism.

Coordinatively saturated $RIr(PMe_3)_4$ (**35**, R = H; **31**, R = C_6H_5) react unusually fast with water and methanol. The products are cationic, and have the OR^- group as the outer sphere anion. Heating solid *cis*-$[H_2Ir(PMe_3)_4](OH)$ (**18**) under vacuum regenerated **35**. Excess PMe_3 did not slow down the reaction. Our results indicate that water and methanol behave here as acids and protonate the

most basic ligand (R).

b. Transformations Inside The Coorhination Sphere

The transformations within the coordination sphere of the hydrido-hydroxo or -alkoxo products were studied in detail. The mechanism of β-H elimination from metal alkoxides was elucidated (including post rate determining steps) and compared to the analogous transformation in metal-alkyls. We also observed an unprecedented mechanistic type of aldehyde expulsion from a metal alkoxide. α-H elimination from coordinated hydroxides of late transition metal complexes was suggested for the first time.

The octahedral alkoxo complexes *mer–cis*–$HIr(OR)Cl(PR_3')_3$ (R = Me, Et, i-Pr; R′ = Me, Et; H *trans* to Cl) decomposed at room temperature in an alcohol/benzene solution forming the dihydrido products *mer–cis*–$H_2IrCl(PR_3')_3$ and the corresponding aldehyde or ketone. The reaction rate was found to be of first order in the iridium complex and of 1.33 order in the alcohol, which served as a catalyst. The rate depended on the nature of the phosphine (PEt_3 > PMe_3), on the alkyl substituent of the alkoxide (Me > Et >> i-Pr) and on the medium (benzene > N-methyl-pyrrolidone) but was not affected by excess phosphine. The activation parameters obtained for the decomposition of *mer–cis*–$HIr(OCH_3)Cl(PMe_3)_3$ (2) are: $\Delta H^{\ddagger}_{obs}$ = 24.1(18) kcal mol^{-1}; $\Delta S^{\ddagger}_{obs}$ = 0.6(59) e.u.; $\Delta G^{\ddagger}_{obs}$ (298°K) = 23.9(36) kcal mol^{-1}. The kinetic isotope effect (combined primary and secondary effects) for the decomposition of *mer–cis*–$DIr(OCD_3)Cl(PMe_3)_3$ at 22°C was 2.45(10) and the secondary kinetic isotope effect for the decomposition of $DIr(OCH_3)Cl(PMe_3)_3$ at 22°C was 1.10(6). Both $DIr(OCH_3)Cl(PMe_3)_3$ and $HIr(OCD_3)Cl(PMe_3)_3$ produced only the two *mer-cis* isomers of $HDIrCl(PMe_3)_3$, but in different ratios.

The following steps are involved in the β–hydride elimination process: (a) pre-equilibrium generation of a free coordination site by chloride dissociation, which is induced by hydrogen bonding of a methanol molecule to the chloride; (b) irreversible rate determining β–C–H cleavage through the *sterically* favored transition state; (c) facile, irreversible dissociation of the aldehyde; (d) ligand rearrangement and (e) irreversible reassociation of the chloride. Selective deuterium labeling enables the elucidation of a competing minor mechanism through the *electronically* favored transition state, operative for the trimethylphosphine complex only. Our study made it possible to point out why

O-H cleavage is rate determining for the β-H elimination from metal alkoxides while either ligand dissociation or olefin detachment are the slow step during β-H elimination from metal alkyls.

The expulsion of $[CH_2O]_x$ from *mer-trans*-$HIr(OMe)(C_6H_5)(PMe_3)_3$ (**20**) generates *mer-trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**33**). The activation parameters of the reaction are: $\Delta H^{\ddagger}_{obs}$ = 8.3(10) kcal mol^{-1}; $\Delta S^{\ddagger}_{obs}$ = -46.8(35) e.u.; $\Delta G^{\ddagger}_{obs}$ (298°K) = 22.2(20) kcal mol^{-1}. They are substantially different from those obtained for the analogous decomposition of **2**. The kinetic isotope effect (combined primary and secondary effects) for the decomposition of *mer–trans*–$DIr(OCD_3)(C_6H_5)(PMe_3)_3$ at 22°C was 3.17(7). Decomposition of *mer–trans*–$DIr(OCH_3)(C_6H_5)(PMe_3)_3$ yields only *mer-trans*-$HDIr(C_6H_5)(PMe_3)_3$. The deuteride is not incorporated neither into the aldehyde nor into the phenyl ring of the product. Decomposition of (**20**) in presence of excess $P(CD_3)_3$ does not lead to incorporation of any labeled phosphine into the product. **33** is the least stable isomer of this compound. It undergoes slow isomerization to the *mer-cis* isomer. The facial isomer was prepared separately, and was found stable.

Our results unequivocally demonstrate that the generally accepted mechanism for β-hydride elimination from metal alkoxides (as from **2**) does not prevail for the decomposition of **20**, since no free coordination site is generated on **20-**, while the alkoxide is bound. The suggested pathway for the reaction involves: (a) dissociation of the alkoxide; (b) η^2-binding of a C-H bond of either a free methanol molecule, or of the dissociated alkoxide and (c) expulsion of the aldehyde, possibly with the support of hydrogen bonding to the dissociated alkoxide or from neighboring methanol molecules.

We observed the decarbonylation of methanol by $(C_8H_{14})IrCl(PMe_3)_3$ (**1**). Unlike other reports on this type of reactivity, our system allows isolation of all the intermediates, and the separate examination of each mechanistic step.

c. alpha-H Elimination from O-H Groups.

This is an important, rarely observed fundamental process, which has bearings pon the development of new catalysis based on water. we have discovered and studied such a process with palladium complexes.

$(TMEDA)Pd(C_6H_5)(OH)$ (**53**) decomposed at room temperature in benzene, toluene or THF, as well as at 70°C in solid state yielding benzene, biphenyl, free

TMEDA, metallic palladium, water, and probably oxygen. A constant 1:1 water to biphenyl ratio was obtained. The benzene to biphenyl ratio was medium dependent, and increased with the addition of water or water + KOH and upon changing from solution to solid state. The iodo analog (TMEDA)Pd(C_6H_5)I (**55**) was found stable even at elevated temperatures. Only addition of KOH caused its slow decomposition, probably via **53** generated *in situ*. No biphenyl was obtained in this decomposition. The kinetic deuterium isotope effect at 90°C for the decomposition of **53** generated *in situ* is unusually large (~25). Decomposition of (TMEDA)Pd(C_6H_5)(OD) yielded C_6H_5D. No deuterium was incorporated into TMEDA or biphenyl.

It is clear from the results that two competing reactions take place, one liberating benzene and probably oxygen, the other forming biphenyl, water and probably oxygen. The likely mechanism for the generation of benzene involves: (a) dissociation of the TMEDA at one site; (b) α-H elimination from the coordinated hydroxide, generating benzene and an unstable d^6 palladium oxo species and (c) further decomposition to the observed products. α-H elimination from coordinated hydroxide of a late transition metal complex is suggested here for the first time.

The final products of the decomposition of (DIPPP)Pd(C_6H_5)OH are benzene, metallic palladium, and the bis-oxidized diphosphine. Three intermediates were observed. Two of them are most likely the tris-coordinated (η^2-DIPPP)Pd{η^1-P(i-Pr)$_2$CH$_2$CH$_2$CH$_2$P(O)(i-Pr)$_2$} and the bis-coordinated Pd{η^1-P(i-Pr)$_2$CH$_2$CH$_2$CH$_2$P(O)(i-Pr)$_2$}$_2$. The most reasonable mechanism for this reaction also involves α-H elimination from the coordinated hydroxide. An intriguing feature of this reaction is its stoichiometry, producing two oxygen atoms per coordinated hydroxide. Catalytic oxidation of the phosphine using water as the oxygen source is a likely.

E. Structural features. the concept of H(+)...H(-) interaction.

The structural analysis of the H-Ir-OR complexes has led to two new concepts suggested for the first time: (a) The concept of the H(δ+)···H(δ-) Interaction - a hydrogen bond in which a σ-bond is the hydrogen bond acceptor. (b) Consideration of the known electronic and steric factors is not enough to enable prediction of the relative stability of monomeric octahedral isomers.

The neutron diffraction structure of *cis*-[HIr(OH)(PMe$_3$)$_4$]PF$_6$ (**15**) revealed

two unique features: (a) The intramolecular IrH···HO distance is only 2.40(1) Å. (b) The Ir-O-H angle of 104.4(7)° is significantly smaller than the tetrahedral angle (109.5°). These observations can be rationalized by postulating *an attractive H(δ+)···H(δ-) interaction between the hydridic Ir-H and the electron deficient OH proton.* It can be understood as a hydrogen bond between a proton and a σ M-H bond. It is important in lowering the activation energy for obtaining X^--M^+-(η^2-H_2) from HX-M-H as well as for the reverse heterolytic splitting of dihydrogen.

In *mer-cis*-HIr(OH)Cl(PEt_3)$_3$ (**13**), the hydroxide is engaged in a strong intramolecular hydrogen bond to the chloro ligand. Yet, three methyl protons, one from each PEt_3 group get as close as 2.15 - 2.2 Å to the hydride, forming a hydrophobic cage around it. Importantly, the C-H bonds interacting with the hydride are significantly longer (by 0.1 - 0.2 Å!) than all other C-H bonds of **13**. It is tempting to suggest that this hydrophobic cage is generated by an H(δ+)···H(δ-) interaction between the hydride and each of these protons.

The comparison of seven *cis*-[HIrX(PMe_3)$_4$]$^+$ (X = OH, OMe, SH, Cl, C_6H_5, CH_2OH, H) structures provides a unique chance to compare the electronic and steric effects of one ligand on octahedral geometries. As expected, the Ir-P bond length *trans* to X was exclusively determined by the *trans* effect of X. However, the other structural parameters are clearly affected by the sterics of X, and not by its electronic properties.

An unresolved, fundamental question emerging from this work concerns the relative stability of the two possible isomers of the [HIrX(PMe_3)$_4$]$^+$ complexes (X = weak σ-donor). Since PMe_3 is larger than all the X ligands we have used, the *trans* isomers are predicted to be *sterically* more stable. Likewise, as the hydride has the strongest *trans* influence), and since X has the weakest, *electronic* considerations also lead to the conclusion that *trans* H-Ir-X species should be the most stable isomers. Yet, for the hydroxo, methoxo and chloro complexes we observed *trans* to *cis* isomerization, leaving no doubt that contrary to both electronic and steric arguments, the *cis* H-Ir-X isomer is more stable in all cases we examined (X = OH, OMe, SH, Cl and H_2O). A literature search has shown that many d^6 ruthenium complexes behave similarly. Theoretic calculation are currently under way in order to elucidate the underlying factors.

F. Towards catalytic anti-Markovnikov hydration of olefins

The catalytic anti-Markovnikov hydration of olefins is a thermodynamically feasible process of immense economic potential. However, due to kinetic reasons, it has not been demonstrated.

In Kazakhstan, the group of Prof. Zakumbaeva has observed that the use of bimetallic Rh-Ir/C and Ru-Co/SiO_2 catalysts at high temperature enables water addition to propylene in an anti- Markovnikov fashion to yield n-propanol as the main product, although significant amounts of iso-propanol are also formed. full details are given in the appendix.

Our hydrido-hydroxo complexes are well suited to study the mechanistic aspects of homogeneous water addition to olefins. The complexes *mer-cis*-HIr-$(OCH_2(CH_2)_n\text{-}CH{=}CH_2)Cl(PR'_3)_3$ (R' = Me, Et; n = 1,2,3) include a tethered olefin that can participate in intramolecular migratory insertion. However, they undergo β-hydride elimination. The cyclic ethers that are the expected products of olefin insertion into the Ir-H or Ir-OH bonds followed by C-O reductive elimination were not obtained. Cyclooctene is catalytically deuterated at each of its positions upon reaction at 70°C with *mer-cis*-$DIr(OD)Cl(PMe_3)_3$, demonstrating that migratory insertion of unactivated olefins into the Ir-H bond is a feasible process. We therefore conclude that the C-O bond formation between the alkyl and hydroxide is the limiting step for late transition metal mediated anti-Markovnikov hydration of olefins. Studies are now underway to clarify this point.

G. Reactions of tridentate cationic Pd(II) complexes with olefins and nucleophiles.

This work is described in detail in the attached publication.

6) Impact, Relevance and Technology Transfer

The group at the Weizmann Institute specializes in homogeneous catalysis by metal complexes and in fundamental organometallic chemistry. Prof. Dorfman's group in Kazakhstan specializes in phosphorous chemistry and homogeneous catalysis. Prof. Zakumbaeva's group has expertise in heterogeneous catalysis by metallic systems.

The collaboration between Israel and Kazakhstan has yielded significant scientific results. The mechanistic understanding of fundamental organometallic chemistry, particularly of activation of O–H and N–H bonds, was important for the development of reactions based on P–H bonds in Kazakhstan. The electrochemical experience in Kazakhstan was helpful in the studies on water and alcohol activation at the Weizmann Institute. The knowledge in organometallic synthesis of metal clusters at the Weizmann Institute was relevant to the development of supported mixed metal catalysts for CO_2 and water activation in Kazakhstan. The two scientists from Kazakhstan, who were trained at the Weizmann Institute in 1994 (Drs. Abdreimova and Shapovalova) implemented in Kazakhstan the experimental techniques acquired at the Weizmann Institute for handling highly air-sensitive compounds, for spectroscopic characterization of metal complexes and for the use of special computer programs. Prof. Dorfman was trained at the Weizmann Institute in special techniques for reactions under gas pressure, as well as in-situ IR and NMR spectroscopy under pressure. A medium pressure reactor, constructed at the Weizmann Institute, was given to Kazakhstan and the new techniques were implemented there, increasing substantially the range of reactions studied at the Institute of Catalysis and Electrochemistry in Alma Ata. A modern FT-IR spectrometer, which is essential for the characterization of solids and solutions, was purchased for Kazakhstan and has enhanced significantly their ability to do catalytic research. Special electrochemical cells developed in Kazakhstan were tested at the Weizmann Institute and adapted for catalytic reactions.

The methods for oxidative alkylation of PH_3 by olefins developed in Kazakhstan open up new ways for the utilization of PH_3, a highly toxic compound that is formed in large amounts in the phosphorous production industry in Kazakhstan. The discovered reactions can probably be extended to other compounds containing P–H bonds and are of general synthetic significance

in phosphorous chemistry.

The study of CO_2 with olefins shows that products of addition can be obtained, although the selectivity needs to be increased. The theoretical understanding of the mode of CO_2 binding to bimetallic catalysts is important in this regard. Development of methods for CO_2 utilization are, of course, very desirable.

The studies on O–H activation of alcohols and water by late metal complexes yielded new synthetic organometallic methodologies, the discovery of new fundamental steps in the coordination sphere of metal hydrido-hydroxy complexes and novel structural features. This basic understanding is important for the development of catalysis based on O–H, N–H and P–H olefin insertion into M–H or H–M–OH complexes has been demonstrated, bringing us closer to the goal of selective anti-Markovikov water addition to olefins. Bimetallic heterogeneous catalysts were discovered in Kazakhstan that promote the addition of water to propylene to give n-propanol as the main product. Further studies are aimed at increasing the selectivity of this reaction.

7) Project Activities/Outputs

Four scientists from Kazakhstan have already visited the Weizmann Institute: Profs. Zakumbaeva and Dorfman at the beginning of the project; Drs. Abdreimova and Shapovalova during June 8-September 1994, and Prof. Dorfman visited again during November 19-December 3, 1995. Prof. Milstein visited Kazakhstan in June 2-8, 1994. The training of Drs. Shapovalova and Abdreimova at the Weizmann Institute included techniques in handling highly air-sensitive compounds, vac line technique, advanced NMR and IR spectroscopies and computer modelling. During the visit of Prof. Dorfman at the Weizmann Institute, joint experiments were planned and performed. While here, Prof. Dorfman, performed potentiometric follow-up of reactions involving metal phosphines. He also became acquainted with our glove box techniques, spectroscopic instrumentation and our systems for medium pressure reactions. Electrochemical cells developed in Kazakhstan are tested and adapted at the Weizmann Institute for catalysis research. A medium pressure gas reactor, developed at the Weizmann Institute, was given to the Institute of Catalysis and Electrochemistry in Kazakhstan.

8) Summary of Travel and Training:

Name	Period	Purpose
Prof. G.D. Zakumbaeva	June 16-21, 1993	Attended CDR conference. Visited the WIS.
Prof. Ya. A. Dorfman	June 16-21, 1993	as above
Prof. D. Milstein	June 2-8, 1994	Visited the Institute of Electrochemistry and Catalysis, Alma Ata, Kazakhstan. Lectured there.
Dr. R.R. Abdreimova	June 8 - Sept 28, 1994	Training at the Weizmann Institute
Dr. R.R. Abdreimova Dr.L.B. Shapovalova Prof. D. Milstein	Aug. 21 - 26, 1994	Presented our research at the International Conference on Homogeneous Catalysis, Jerusalem, Israel
Dr.L.B. Shapovalova	June 8 - Sept 28, 1994	Training at the Weizmann Institute
Prof. G.D. Zakumbaeva Prof. Ya. A. Dorfman	October 31-November 2, 1994.	Presented the research at the Japan-FSU Catalysis Seminar, in Tsukuba, Japan
Prof. Ya. A. Dorfman	November 19-December 3, 1995.	Training at the Weizmann Institute

9) Publications

1. M. Portnoy, Y. Ben-David, I. Rousso and D. Milstein, *Organometallics*, 1994, 13, 3465-3469.
Reactions of electron-rich aryl-palladium complexes with olefins. Origin of chelate effect in vinylation catalysis.

2. H.-B. Kraatz and D. Milstein
The Reactivity of Tridentate Cationic Palladium(II) with Olefins and Nucleophiles.
J. Organometal. Chem., 488, 223 (1995) (special issue)

3. Ya. Dorman, R.R. Abdreimova, D.N. Akbaeva, S.M. Aibasova, M.M. Aleshkova, F.H. Faisova, V.N. Stratsyuk, *Proc. 9th Int'l Symp. Homog. Catal.*, Jerusalem, Israel, August 21-26, 1994, pp. 295-296.
Oxidative P–N and P–O bonding of tetraphosphorous with amine and alcohol catalyzed by Cu(II) chlorides

4. O. Blum and D. Milstein. *Proc. 9th Int'l Symp. Homog. Catal.*, Jerusalem, Israel, August 21-26, 1994, pp. 305-306.
Mechanism of O–H cleavage in water and alcohols by Ir(I).

5. O. Blum and D. Milstein,
O–H activation of aliphatic alcohols by Ir(2). Synthesis and mechanism. submitted to *Inorg. Chem.*

6. O. Blum and D. Milstein,
O–H activation by Ir(1) to be submitted to *Inorg. Chem.*

7. Y.A. Dorfman, G.S. Polimbetova and E.J. Aybasov, *J. General Chem.* 1995, 65, 1.
Oxidative alkoxylalkylation and chloroalkylation of phosphine by styrene and alcohol in the presence of mercury (II) chloride.

8. Y.A. Dorfman, G.S. Polimbetova, R.R. Abdreimova, L.V. Levina and D.N. Akbaeva
New oxidtive alkylation, alkoxylation and amination of phosphine and

tetraphosphorous by olefins, alcohols and amines in the presence of Hg(II), Pd(II), Pt(IV), Cu(II) complexes

9. G. Zakumbaeva and L.B. Shapovalova, Proceedings of the Japan-FSU Catalysis Seminar, October 31-November 2, 1994, Tsukuba, Japan, pp. 78-83.

10. Y.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova and L.V. Levina
Novel oxidative C–P, O–P, N–P coupling of alcohols, olefins, amines and nitriles to P_4 and PH_3 catalyzed by transition metal complexes
Proceedings of the 13th International Conference on Phosphorous Chemistry, Jerusalem, Israel, July 16-21, 1995, p.7.

11. G.D. Zakumbaeva and L.B. Shapovalova
Interation of CO_2 with olefins
Proceedings of the Japan-FSU Catalysis Seminar, October 31-November 2, 1994, Tsukuba, Japan, pp. 28-33.

12. Y. Dorfman and G.S. Polimbetova
Novel catalytic reactions of oxidative P–C, P–O, P–N coupling of phosphine to alcohols, olefins, quinones, amines and nitriles to be submitted

13. G.D. Zakumbaeva and L.B. Shapovalova
Proceedings of the Conference on Modern Trends in Chemical Kinetics and Catalysis, Novosibirsk, Russia, November 21-24, 1995.

10) Future Work

Future work on based on the results obtained in this project is planned.. Emphasis will be placed on (a) catalytic reaction of olefins with water, in solution and in the gas phase. This will be done in parallel at the Weizmann Institute (solution chemistry) and in Kazakhstan (gas phase). (b) Extension of the synthetic methodology involving PH_3 and olefins. (c) Catalytic addition of CO_2 to olefins, based on the newly discovered Co/Ru catalyst.

11) Appendix

Reprints and manuscripts resulting from this work.