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First example of catalytic decarbonylation and metathesis reactions of .alpha.-ketophosphonates promoted by a palladium complex

Hiroshi. Nakazawa, Yuko. Matsuoka, Hideaki. Yamaguchi,
Toshiaki. Kuroiwa, Katsuhiko. Miyoshi, and Hayami. Yoneda

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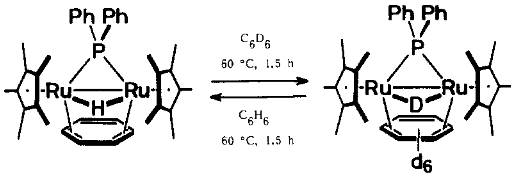
C(4)–C(9) and C(7)–C(8) bond lengths were 1.442 and 1.428 Å, respectively, which were in the range observed for a variety of transition-metal η^2-olefin complexes.[15] By contrast, a C(15)–C(6) distance of 1.332 Å was consistent with that of an isolated carbon–carbon double bond. Some precedent for such bond localization has appeared.[10,16] While C=C and C—C bond lengths of uncoordinated 1,3-butadiene are 1.334 and 1.476 Å, respectively, those in the η^4-diene moiety (C(4)–C(9)–C(8)–C(7)) are 1.435 (average) and 1.460 Å, respectively. The results indicate bond delocalization over the η^4-diene moiety in coordinated benzene as observed in several 1,3-diene complexes.[17] The benzene ring in **2** is nonplanar. The torsional angle between the C(4)–C(9)–C(8)–C(7) plane and the C(4)–C(5)–C(6)–C(7) plane is ca. 12°, and the noncoordinated double bond is bent away from the ruthenium centers.

The formation of **2** would reasonably be elucidated by a sequence of reactions depicted below. Reductive elimination of H_2 from **1** and coordination of PPh_3 would form an intermediary dihydrido monophosphine complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(PPh_3)Ru(\eta^5\text{-}C_5Me_5)$. Activation of the P–C bond of the coordinated PPh_3 by one of the ruthenium centers would be expected to yield the μ-phosphido species $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}PPh_2)Ru(C_6H_5)(\eta^5\text{-}C_5Me_5)$, which would then undergo reductive elimination of benzene and subsequent coordination of the benzene in a μ-η^2:η^2-mode to give **2**.

For the cluster-mediated P–C bond cleavage of tertiary phosphine, similar mechanism has been proposed.[18]

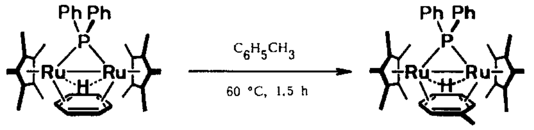
As mentioned above, ^1H NMR study of **2** at the elevated temperature showed that the μ-benzene ligand was not fluxional at least below 80 °C. Slow ligand exchange between μ-benzene and uncoordinated benzene was, however, observed upon heating the benzene solution of **2**. When a solution of **2** in C_6D_6 was warmed at 60 °C for 1.5 h, the deuterated complex **2**-d_7 was formed exclusively (eq 2).



(2)

Complex **2**-d_7 was isolated in 82% yield and was characterized by means of ^2H and ^{13}C NMR and infrared spectroscopy. Resonances for the μ-C_6D_6 and deuteride ligands appeared at δ 5.20 (m, 2 D), 2.77 (m, 2 D), 2.70 (m, 2 D), and −16.5 (d, J_{PD} = 5.0 Hz, 1 D), respectively, in the $^2H\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum showed three triplets for the μ-C_6D_6 ligand at δ 123.7 (t, J_{CD} = 23.1 Hz), 47.3 (t, J_{CD} = 23.8 Hz), and 45.9 (t, J_{CD} = 22.6 Hz). Coordination of the C_6D_6 molecule was further confirmed on the basis of ν_{CD} bands at 2295, 2281, and 2228 cm^{-1} observed in the infrared spectrum. Treatment of the deuterated complex **2**-d_7 in C_6H_6 at 60 °C for 1.5 h again afforded **2** quantitatively.

Replacement of the coordinated benzene by toluene leading to **3** was also observed by means of ^1H NMR spectroscopy upon heating complex **2** in toluene at 60 °C (eq 3).[19] Monitoring the conversion of **2** or **3** to **2**-d_7 at 60 °C in 10-min intervals by means of ^1H NMR spectroscopy showed that the rate of $Ru_2(C_6H_6)/Ru_2(C_6D_6)$ exchange was comparable to that of $Ru_2(C_6H_5CH_3)/Ru_2(C_6D_6)$ exchange and that the rate of η^4-arene exchange was much faster than that of Ru_2H/Ru_2D exchange.



(3)

These results strongly imply that the conversion of **2** to **2**-d_7 proceeds via initial $Ru_2(C_6H_6)/Ru_2(C_6D_6)$ exchange followed by the cleavage of C–H bond of coordinated benzene.

Further mechanistic studies pertaining to the H/D exchange will be reported in due course.

Acknowledgment. Support from the Ministry of Education, Science and Culture of the Japanese Government (No. 63550618) is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic data from the X-ray study, atomic coordinates, interatomic distances and angles, and thermal parameters (11 pages); a listing of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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[19] **3**: ^1H NMR (C_6D_6) δ −16.7 (d, J_{PH} = 40.3 Hz, 1 H, Ru–H–Ru), 1.37 (s, 3 H, $C_6H_5CH_3$), 1.59 (s, 15 H, C_5Me_5), 1.67 (s, 15 H, C_5Me_5), 2.58 (d, J_{HH} = 7.4 Hz, 1 H, $C_6H_5CH_3$), 2.65 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6H_5CH_3$), 2.76 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6H_5CH_3$), 2.82 (dd, J_{HH} = 7.4 and 5.5 Hz, 1 H, $C_6H_5CH_3$), 5.31 (d, J_{HH} = 5.5 Hz, 1 H, $C_6H_5CH_3$), 6.72–7.76 (m, 10 H, PPh_2); ^{13}C NMR (C_6D_6) δ 10.3 (q, J_{CH} = 126.5 Hz, C_5Me_5), 10.6 (q, J_{CH} = 126.2 Hz, C_5Me_5), 45.8 (d, J_{CH} = 162.4 Hz, η^4-toluene), 46.2 (d, J_{CH} = 154.6 Hz, η^4-toluene), 48.4 (d, J_{CH} = 153.6 Hz, η^4-toluene), 50.2 (d, J_{CH} = 156.5 Hz, η^4-toluene), 93.3 (s, C_5Me_5), 93.5 (s, C_5Me_5). Resonances for aromatic carbons on PPh_2 and toluene ligands could not be assigned.

First Example of Catalytic Decarbonylation and Metathesis Reactions of α-Ketophosphonates Promoted by a Palladium Complex

Hiroshi Nakazawa,*,[1] Yuko Matsuoka, Hideaki Yamaguchi,[2], Toshiaki Kuroiwa,[2] Katsuhiko Miyoshi, and Hayami Yoneda*,[3]

Department of Chemistry, Faculty of Science
Hiroshima University, Hiroshima 730, Japan

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Summary: Arylketophosphonates and alkylketophosphonates undergo decarbonylation in toluene-reflux conditions, in the presence of a catalytic amount of a palladium complex, to afford arylphosphonates and alkylphosphonates, respectively. Evidence is presented for a metathesis reaction of α-ketophosphonates ($RC(O)P(O)(OR)_2 + R'C(O)P(O)(OR')_2 \rightleftharpoons RC(O)P(O)(OR')_2 + R'C(O)P(O)(OR)_2$), catalyzed by a palladium complex, which takes place prior to the observed decarbonylation reaction.

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[1] To whom correspondence should be addressed.

[2] Present address: Mitsui Petrochemical Industry, LTD., Wakicho, Kuga-gun, Yamaguchi, 740, Japan.

[3] Present address: Department of Fundamental Natural Science, Okayama University of Science, Okayama, 700, Japan.

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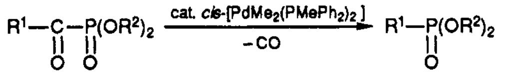
The phosphorus–carbon bond is known to be relatively strong and therefore less readily cleaved as compared with phosphorus–halogen, phosphorus–nitrogen, and phosphorus–hydrogen bonds.[4] Recent reports of phosphorus–carbon bond activation by transition-metal complexes have generated a great deal of interest in the field of transition-metal and phosphorus chemistry.[5] However, most reports to date are concerned with phosphorus–aryl carbon bond scission in triarylphosphines. Only a limited number of examples with stoichiometric P–C (except the aryl carbon) bond cleavage have been found.[6] Herein we report an unprecedented, palladium-catalyzed P–C bond cleavage which results in decarbonylation and metathesis of α-ketophosphonates.

In a typical procedure, $(Ph)C(O)P(O)(OEt)_2$ (136 μL, 164 mg, 0.679 mmol) was added to a solution of *cis*-$[PdMe_2(PMePh_2)_2]$ (1) (73 mg, 0.136 mmol) in 3 mL of toluene. The reaction mixture was heated at reflux for 0.2 h to give $(Ph)P(O)(OEt)_2$ (100% yield based on $(Ph)C(O)P(O)(OEt)_2$). The disappearance of the reactant and the formation of the product were confirmed by gas chromatography and ^{31}P NMR measurements.

The catalytic activity of related palladium complexes has been examined, and on the basis of the following results, we suggest that the catalytically active species is a 14-electron Pd(0) complex, "PdL_2": (i) complex 1, *trans*-$[PdMe_2(PMePh_2)_2]$, and $Pd(styrene)(PMePh_2)_2$ all exhibit similar catalytic activity,[7] whereas *trans*-$[PdMe_2(PMe_2Ph)_2]$ and $PdMe_2(dppe)$ showed slightly lower activity;[8] (ii) $Pd(PPh_3)_4$, being in equilibrium with $Pd(PPh_3)_3$ and $Pd(PPh_3)_2$, required 48 h to complete the decarbonylation;[9] (iii) $Pd(PCy_3)_2$ also exhibited catalytic activity, although it required 75 h to achieve a 60% yield; (iv) $PdCl_2(PPh_3)_2$, $PdCl_2(NCPh)_2$, and $Pd(acac)_2$ which do not form 14-electron Pd(0) species upon heating showed no catalytic activity.[10]

In order to obtain additional support for a 14-electron Pd(0) catalyst, the reaction of 1 with 5 equiv of $(Ph)C(O)P(O)(OEt)_2$ was carried out in the presence of 5 equiv of $PMePh_2$. Under these conditions 72 h were required to finish the decarbonylation, whereas in the absence of excess phosphine the reaction was completed in 0.2 h. This result is consistent with our assumption that "PdL_2" is the active species. The decarbonylation is presumably initiated by an oxidative addition of a C–P bond between the acyl and phosphonate groups in α-ketophosphonates to the "PdL_2" species.[11]

Equation 1 shows the decarbonylation results for various α-ketophosphonates when 1 is employed as a catalyst. Both arylketophosphonates and alkylketophosphonates undergo decarbonylation, though in an extremely low yield for ethylketophosphonates. These reactions were carried out under the same conditions stated above (in refluxing toluene in the presence of 20 mol % of 1) except the reaction time. It took ca. 0.2 h for arylketophosphonates but ca. 72 h for alkylketophosphonates to drive the reaction to completion.

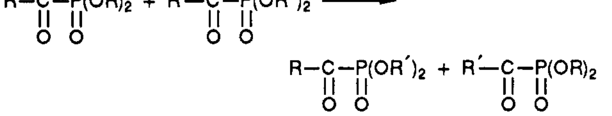


$$R^1-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR^2)_2 \xrightarrow[-CO]{\text{cat. } cis\text{-}[PdMe_2(PMePh_2)_2]} R^1-\underset{\underset{O}{\|}}{P}(OR^2)_2 \tag{1}$$

R^1	R^2	yield
= Ph	= Et	= 100%
= *p*-tolyl	= Et	= 100%
= *p*-MeO–phenyl	= Et	= 72%
= *p*-Cl–phenyl	= Et	= 65%
= Ph	= Me	= 76%
= Me	= Et	= 55%
= Me	= Me	= 43%
= Et	= Et	= 9%
= Et	= Me	= 5%

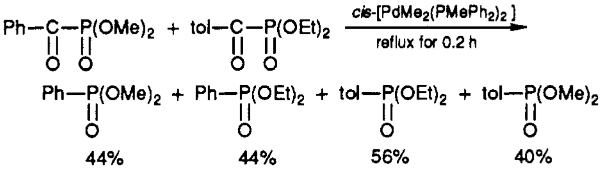
Although decarbonylations are known for aldehydes, acyl halides,[12] acyl cyanides,[13] and thiol esters,[14] which involve C(O)–H, C(O)–halogen, C(O)–CN, and C(O)–S bond cleavage, respectively, decarbonylation via C(O)–P bond fission has not been reported so far. The results reported here represent the first such examples.

We have also found evidence for an α-ketophosphonates metathesis reaction prior to the observed decarbonylation (eq 2).



$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR)_2 + R'-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR')_2 \xrightarrow{\text{Pd cat.}} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR')_2 + R'-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR)_2 \tag{2}$$

A crossover experiment was performed involving equimolar amounts of $(Ph)C(O)P(O)(OMe)_2$ and $(tol)C(O)P(O)(OEt)_2$ (tol = *p*-tolyl) and a catalytic amount of 1. The product distribution consisted of equimolar amounts of $(Ph)P(O)(OMe)_2$, $(Ph)P(O)(OEt)_2$, $(tol)P(O)(OEt)_2$, and $(tol)P(O)(OMe)_2$ (eq 3).[15] In a separate experiment, it was confirmed that $(Ph)P(O)(OEt)_2$ and $(tol)P(O)(OMe)_2$ are not derived from $(Ph)P(O)(OMe)_2$ and $(tol)P(O)(OEt)_2$ in the presence of 1. It is therefore reasonable to assume that $(Ph)P(O)(OEt)_2$ and $(tol)P(O)(OMe)_2$ are derived from the decarbonylation of $(Ph)C(O)P(O)(OEt)_2$ and $(tol)C(O)P$-



$$Ph-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OMe)_2 + tol-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OEt)_2 \xrightarrow[\text{reflux for 0.2 h}]{cis\text{-}[PdMe_2(PMePh_2)_2]} \underset{44\%}{Ph-\underset{\underset{O}{\|}}{P}(OMe)_2} + \underset{44\%}{Ph-\underset{\underset{O}{\|}}{P}(OEt)_2} + \underset{56\%}{tol-\underset{\underset{O}{\|}}{P}(OEt)_2} + \underset{40\%}{tol-\underset{\underset{O}{\|}}{P}(OMe)_2} \tag{3}$$

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(7) $(Ph)C(O)P(O)(OEt)_2$ was converted into $(Ph)P(O)(OEt)_2$ in 100% yielded by refluxing the toluene solution containing 20 mol % of the palladium complex based on $(Ph)C(O)P(O)(OEt)_2$ for 0.2 h.

(8) Yields of 69% and 60% by refluxing *trans*-$[PdMe_2(PMe_2Ph)_2]$ and $PdMe_2(dppe)$ for 2 and 5 h respectively, where dppe stands for 1,2-bis(diphenylphosphino)ethane.

(9) 52% yield.

(10) 100% of $(Ph)C(O)P(O)(OEt)_2$ was recovered in each case.

(11) Recently we could isolate the complexes $PdL_2\{C(O)R\}\{P(O)(OR)_2\}$ in the reaction of PdR_2L_2 with $RC(O)P(O)(OR)_2$, and the complexes showed the catalytic ability of decarbonylation toward α-ketophosphonates. The results will be reported elsewhere.

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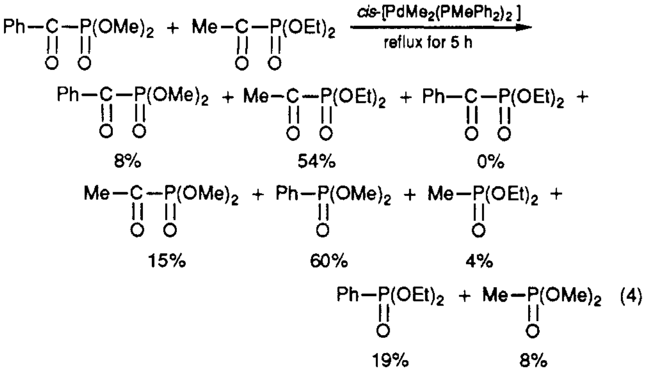
(13) Murahashi, S.-I.; Naota, T.; Nakajima, N. *J. Org. Chem.* **1986**, *51*, 898.

(14) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1987**, *28*, 6321.

(15) The % expresses the % yield of the phosphonates. If the two kinds of α-ketophosphonates are completely converted into the four kinds of phosphonates with equal distribution, the % expression should be 50%:50%:50%:50%.

(O)(OMe)$_2$, respectively, both of which may be generated by metathesis between (Ph)C(O)P(O)(OMe)$_2$ and (tol)C(O)P(O)(OEt)$_2$.

Additional results were obtained from the reaction of (Ph)C(O)P(O)(OMe)$_2$ and (Me)C(O)P(O)(OEt)$_2$ with a catalytic amount of 1 (refluxing in toluene for 5 h) (eq 4).



(4)

In addition to the starting α-ketophosphonates and their direct decarbonylation products, three kinds of phosphorus compounds, (Ph)P(O)(OEt)$_2$, (Me)C(O)P(O)(OMe)$_2$, and (Me)P(O)(OMe)$_2$, were detected. Although the other expected product of the metathesis, (Ph)C(O)P(O)(OEt)$_2$, was not detected, the decarbonylation product, (Ph)P(O)(OEt)$_2$ was observed.

In a similar fashion the reaction of (Et)C(O)P(O)(OMe)$_2$ and (Me)C(O)P(O)(OEt)$_2$ in the presence of 1 (refluxing in toluene for 24 h) leads to the formation of two additional α-ketophosphonates and four phosphonates in low yield.[16]

Investigations into the mechanism of transition-metal-promoted decarbonylation and metathesis of α-ketophosphonates are currently under way.

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Supplementary Material Available: A table of ^{1}H and ^{31}P NMR data for phosphonates (1 page). Ordering information is given on any current masthead page.

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[16] The yields of the methathesis products and the decarbonylation products were 1–8%.

Catalytic and Stoichiometric Formation of Cyclooctatetraenes from Soluble Nickel Complexes

Christophe J. Lawrie, Kevin P. Gable, and Barry K. Carpenter*

Baker Laboratory, Department of Chemistry
Cornell University, Ithaca, New York 14853-1301

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Summary: A benzene-soluble, catalytically active material of composition $\{(PhCC)_2Ni\}_{12-13}$ is isolated by gel-permeation chromatography from the Reppe cyclotetramerization of phenylacetylene with Ni(acac)$_2$/CaC$_2$ or NiBr$_2$/CaC$_2$. Possible steps in the catalytic process are modeled in stoichiometric reactions.

The Reppe reaction, producing cyclooctatetraene (COT) from acetylene with a variety of nickel catalysts, is now more than 40 years old.[1] Despite that, it is a reaction for which mechanistic details are still being investigated.[2-4]

The purpose of this communication is to report the isolation and independent preparation of a hydrocarbon-soluble, oligomeric catalyst from the Reppe reaction of phenylacetylene and to describe some stoichiometric modeling of its reactions.

A study on the catalytic cyclooligomerization of phenylacetylene to 1,2,4-triphenylbenzene and 1,3,5,8-cyclooctatetraene (1)[5] by Ni(acac)$_2$/CaC$_2$ or Ni(Br)$_2$/CaC$_2$ revealed formation of a benzene-soluble material that had an elemental composition corresponding to $\{(PhC_2)_2Ni\}_n$. This material, which could be isolated by gel-permeation chromatography, had a molecular weight of 3250 ± 290, corresponding to a value near 13 for *n* in the above formula. Various preparations of the material had magnetic properties ranging from diamagnetism to weak paramagentism, with the maximum magnetic moment, as determined by the Evans' method,[6] being 3.77 μ_B.

The material was shown to be an active catalyst, leading to triphenylbenzene and Ph$_4$-COT formation from phenylacetylene, without any apparent induction period.[7] Its isolation from the chromatography presumably precludes catalysis by adventitious colloidal nickel. An apparently identical material (as judged by IR and elemental composition) could be prepared in 60% yield by reaction of 2 equiv of PhCCLi with (1,2-dimethoxyethane)NiCl$_2$ in THF at −70 °C.[8]

Hydrolysis of the catalyst with concentrated aqueous HCl afforded a tarry oligomeric hydrocarbon but did not yield any phenylacetylene, suggesting that the catalyst was not an oligomer of nickel(II) bis(phenylacetylide). This conclusion was reinforced by the observation that treatment with bis(diphenylphosphino)ethane (diphos) resulted in the formation of (diphos)$_2$Ni^0 (corresponding to about 30% of the theoretical amount of Ni). Preparation of the catalyst with C$_6$D$_5$CCLi and reaction with 5 equiv of C$_6$H$_5$CCH resulted in formation of triphenylbenzene and Ph$_4$-COT containing ≤1% deuterium again suggesting that the orginal phenylacetylide unit was no longer present in that form in the catalyst.

When the catalyst was used to oligomerize (*o*-allylphenyl)acetylene, the resulting tetramer (formed catalytically as a mixture of stereoisomers and accompanied by several minor products of as yet unknown structure) was

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[1] Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1.

[2] Schrauzer, G. N. *Chem. Ber.* **1961**, *94*, 1403.

[3] Vollhardt, K. P. C.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5470.

[4] Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185 and references therein.

[5] A substituted COT has to be numbered in a way that specifies the particular bond-shift isomer. In the present case, evidence from the stoichiometric reactions suggests that it is undesirable to have a double bond between neighboring phenyl groups in a Ph$_4$-COT, which is why the particular isomer shown in Scheme I has been selected. The possibility that it is really 1,2,4,6-tetraphenylcyclooctatetraene cannot be rigorously excluded, however.

[6] Evans, D. *J. Chem. Soc.* **1959**, 2003.

[7] In a typical result, 5 mg of the catalyst converted a solution of 120 mg of phenylacetylene in 1 mL of benzene to 8.9 mg of triphenylbenzene and 98.9 mg of Ph$_4$-COT after 15 h at 70 °C.

[8] It is possible that this material is the same as that prepared by Nast et al. (Nast, R.; Vester, K.; Griesshammer, H. *Chem. Ber.* **1957**, *90*, 2678), although the magnetic susceptibility determined by these workers would suggest a higher magnetic moment than that determined in the present work. No study of catalytic activity with acetylenes was reported by the Nast group. It may also be that the Reppe catalyst prepared from reaction of nickel atoms with phenyl acetylene is related to the present material (Simons, L. H.; Lagowski, J. J. *Fundam. Res. Homogeneous Catal.* **1978**, *2*, 73).

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